

**PROCESS DESIGN MANUAL
FOR
SULFIDE CONTROL IN
SANITARY SEWERAGE SYSTEMS**

**U. S. ENVIRONMENTAL PROTECTION AGENCY
Technology Transfer**

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FOREWORD

The formation of the United States Environmental Protection Agency marked a new era of environmental awareness in America. This Agency's goals are national in scope and encompass broad responsibility in the area of air and water pollution, solid wastes, pesticides, and radiation. A vital part of EPA's national water pollution control effort is the constant development and dissemination of new technology for wastewater treatment systems.

It is now clear that only the most effective design and operation of wastewater treatment systems, using the latest available techniques, will be adequate to meet the future water quality objectives and to ensure continued protection of the nation's waters. It is essential that this new technology be incorporated into the contemporary design of waste treatment systems to achieve maximum benefit of our pollution control expenditures.

The purpose of this manual is to provide the engineering community and related industry a new source of information to be used in the control of corrosion and noxious conditions resulting from hydrogen sulfide in existing sewerage systems, and in the development of designs for new systems so as to keep them free from these problems.

Much of the information presented is based upon research sponsored by the U. S. EPA, including investigations of the occurrence and effects of sulfide in existing sewerage systems, and the performance of equipment and procedures in actual use for sulfide control. The performance data given should be used as a guide and should be tempered with sound engineering judgment based on a complete analysis of the specific application.

This manual is one of several available through the Technology Transfer Office of EPA to describe recent technological advances and new information. Future editions of this manual will be issued as warranted by advancing state-of-the-art to include new data as it becomes available, and to revise design criteria as additional full-scale operational information is generated.

CHAPTER 1

INTRODUCTION

1.1 Background

One characteristic by which sanitary sewage is known to the public is its potential for creating odor nuisances. Sometimes it is the odors escaping from sewer manholes that cause complaints; more commonly, the source is a wastewater treatment plant. Yet there are wastewater treatment plants that are free from this stigma. Techniques to prevent odor nuisances are available, and if there is a commitment to construct odor-free sewage works, it can be done.

The main cause of odors in sewerage systems is hydrogen sulfide, or H_2S , a gas detectable in very low concentration. Hydrogen sulfide is also noted for its toxicity and for its ability to cause corrosion of various materials used in sewer construction.

Much research has been done on various aspects of the sulfide problem in the last three decades. Beside extensive studies in the United States, important contributions have been made by engineers in Australia under the leadership of a Standing Committee of the principal sewerage authorities. In South Africa, research has been done on the corrodability of concrete under conditions that may develop in sewers (1). The first attempt at a comprehensive treatise on the sulfide problem was published as a joint effort of the engineers in Australia (2). Despite the completion of that work, there is more that can be added on the basis of results of recent research in the United States.

1.2 Purpose

A comprehensive design manual is necessary to bring together the information now available into a form convenient for use by engineers who are designing sewers or who are faced with the need to apply sulfide control procedures in existing sewers. This Manual is intended to satisfy that need. It is based principally upon sources of information in the cited references. Some of the data, however, including that developed by research and development projects of the U.S. EPA, have not yet been published elsewhere, and some of the deductions were developed from published and unpublished data in the course of the preparation of the Manual.

Sulfide control is now a well developed technology. Continuing advances in basic knowledge and in the development of control procedures are to be expected, but application of the art in its present state, as set forth in this Manual, will overcome sulfide-producing tendencies in existing systems and provide an understanding of how systems can be designed to minimize such problems in the future.

1.3 References

1. Stutterheim, N., and Van Aardt, J. H. P., *Corrosion of Concrete Sewers and Some Remedies*, South African Industrial Chemistry, No. 10, (1953).
2. Thistlethwayte, D. K. B., *Control of Sulphides in Sewerage Systems*, Butterworths Pty. Ltd., Melbourne, Australia (1972), and Ann Arbor Science Publishers Inc., Ann Arbor, Michigan (1972).

CHAPTER 2

CHARACTERISTICS AND PROPERTIES OF HYDROGEN SULFIDE

2.1 Forms of Sulfide in Wastewaters

The term sulfide refers to inorganic sulfur in its most reduced state, that is, with a valence of minus two. In wastewaters, sulfide is a mixture of:

1. Insoluble metallic sulfides. There is evidence that wastewaters may contain several iron sulfides: pyrrhotite (variable from FeS to Fe_4S_5), smythite (Fe_3S_4), and pyrite or marcasite (FeS_2). In addition, small amounts of sulfides of zinc, copper, lead, cadmium, and other metals may be present insofar as the wastewater contains any such metals.
2. Dissolved sulfide. This is a mixture of H_2S and HS^- (read HS ion) existing in equilibrium with hydrogen ions, as shown by the following equation:



The secondary sulfide ion, $\text{S}^{=}$, does not exist as a significant fraction of the sulfide content except at very high pH. For example, less than 0.05 percent of the dissolved sulfide is present as $\text{S}^{=}$ at pH 11, and less than 0.5 percent is present at pH 12. The proportion of H_2S as a function of pH is discussed in the next section.

There are also organic sulfur compounds in which the sulfur is arbitrarily assigned a valence of minus two, and which may be called *organic sulfides*. They do not respond to the analytical tests used to measure inorganic sulfide, and they do not have the same significance. The volatile organic sulfur compounds, however, are very important odor components in wastewater. They are principally of three types: the thiols, also called mercaptans, containing an $-\text{SH}$ group (example, methanethiol, CH_3-SH); the thioethers, also called sulfides, in which two organic radicals are attached to sulfur (example, dimethylthioether, $\text{CH}_3-\text{S}-\text{CH}_3$); and the disulfides, with two organic radicals joined to a pair of sulfur atoms (example, dimethyl disulfide, $\text{CH}_3-\text{S}-\text{S}-\text{CH}_3$). There are also nonvolatile sulfur compounds that cause none of the problems associated with the volatile compounds, but that may break down by biological action to yield inorganic sulfide. Naturally occurring compounds of this type in wastewater are principally the albuminoid proteins.

2.2 Physical-Chemical Properties of Hydrogen Sulfide

Hydrogen sulfide is normally a gas, liquefying at -62°C under one atmosphere pressure,

or at 25°C under a pressure of 20 atmospheres. At 25°C and one atmosphere pressure, a liter of H₂S weighs 1.40 grams, of which 1.31 grams are sulfur. It is moderately soluble in water, more so than carbon dioxide and most other common gases. Table 2-1 shows the solubility, in milligrams per liter of sulfide, at one standard atmosphere pressure, and also the partial pressure of H₂S over a solution of 1 mg/l of H₂S (as S), expressed in millionths of an atmosphere, which is the same as parts per million of H₂S by volume in the air when the total pressure is one standard atmosphere. At a high altitude, the total pressure is diminished, but the partial pressure of H₂S over water with 1 mg/l of H₂S remains the same. Consequently the proportions of H₂S in the atmosphere expressed as ppm by volume varies inversely as the atmospheric pressure.

The proportions of H₂S and HS⁻ in the dissolved sulfide fraction in water are primarily a function of pH, and can be calculated most readily from the ionization constant written in the logarithmic form:

$$\log \frac{[HS^-]}{[H_2S]} = pH - pK'$$

where pK' is the negative logarithm of the practical ionization constant as written in the arithmetic form. The chemical formulas appearing in brackets are here used to signify concentrations, which in this case mean concentrations expressed as S.

The value of pK' is influenced by temperature and by the ionic strength of the solution. Sometimes ionic strength is estimated from the "total dissolved solids" or "filterable residue," but in wastewaters the relationship is not very reliable. Wastewaters may contain un-ionized solutes. Also ammonium salts may be present as ions, which are lost when the sample is evaporated. This is especially true in the liquor of digested sludge. A better approximation is obtained from the specific electric conductance. The specific electrical conductance at 25°C, expressed as micromhos/cm, multiplied by 1.35x10⁻⁵ gives a fair approximation of the effective ionic strength, expressed in units of moles per liter.

Table 2-2 shows values of pK' at various concentrations of salts as represented by conductance, based upon the best available data (2). An all-purpose value of pK' for rough estimates is 7.0.

TABLE 2-1

SOLUBILITY OF H_2S IN WATER AT A PRESSURE OF ONE STANDARD ATMOSPHERE (1)

Temp. °C	Solubility milligrams per liter expressed as S	H ₂ S in atmosphere in equilibrium with a solution of 1 mg/l as S	
		partial pressure, millionths of an atmosphere	milligrams per liter of S in the air
0	6648	150	0.214
1	6434	155	0.221
2	6227	160	0.228
3	6028	166	0.235
4	5834	171	0.242
5	5646	177	0.249
6	5465	183	0.256
7	5291	189	0.263
8	5124	195	0.271
9	4964	201	0.279
10	4810	208	0.287
11	4667	214	0.294
12	4529	221	0.302
13	4398	227	0.310
14	4271	234	0.318
15	4150	241	0.326
16	4033	248	0.334
17	3922	255	0.343
18	3816	262	0.351
19	3714	269	0.359
20	3618	276	0.368
21	3523	284	0.376
22	3432	291	0.385
23	3344	299	0.394
24	3258	307	0.403
25	3175	315	0.412
26	3095	323	0.421
27	3018	331	0.430
28	2945	340	0.440
29	2874	348	0.449
30	2806	356	0.459
35	2491	401	0.508
40	2221	450	0.560

TABLE 2-2

LOGARITHMIC PRACTICAL IONIZATION CONSTANTS (pK') FOR HYDROGEN SULFIDE

Specific electrical conductance at 25°C, micromhos per cm	Temperature, °C						
	10	15	20	25	30	35	40
0	7.24	7.17	7.10	7.03	6.96	6.89	6.82
25	7.23	7.16	7.09	7.02	6.95	6.88	6.81
100	7.22	7.15	7.08	7.01	6.94	6.87	6.80
200	7.21	7.14	7.07	7.00	6.93	6.86	6.79
400	7.20	7.13	7.06	6.99	6.92	6.85	6.78
700	7.19	7.12	7.05	6.98	6.91	6.84	6.77
1,200	7.18	7.11	7.04	6.97	6.90	6.83	6.76
2,000	7.17	7.10	7.03	6.96	6.89	6.82	6.75
3,000	7.16	7.09	7.02	6.95	6.88	6.81	6.74
4,000	7.15	7.08	7.01	6.94	6.87	6.80	6.73
5,200	7.14	7.07	7.00	6.93	6.86	6.79	6.72
7,200	7.13	7.06	6.99	6.92	6.85	6.78	6.71
10,000	7.12	7.05	6.98	6.91	6.84	6.77	6.70
14,000	7.11	7.04	6.97	6.90	6.83	6.76	6.69
22,000	7.10	7.03	6.96	6.89	6.82	6.75	6.68
50,000*	7.09	7.02	6.95	6.88	6.81	6.74	6.67

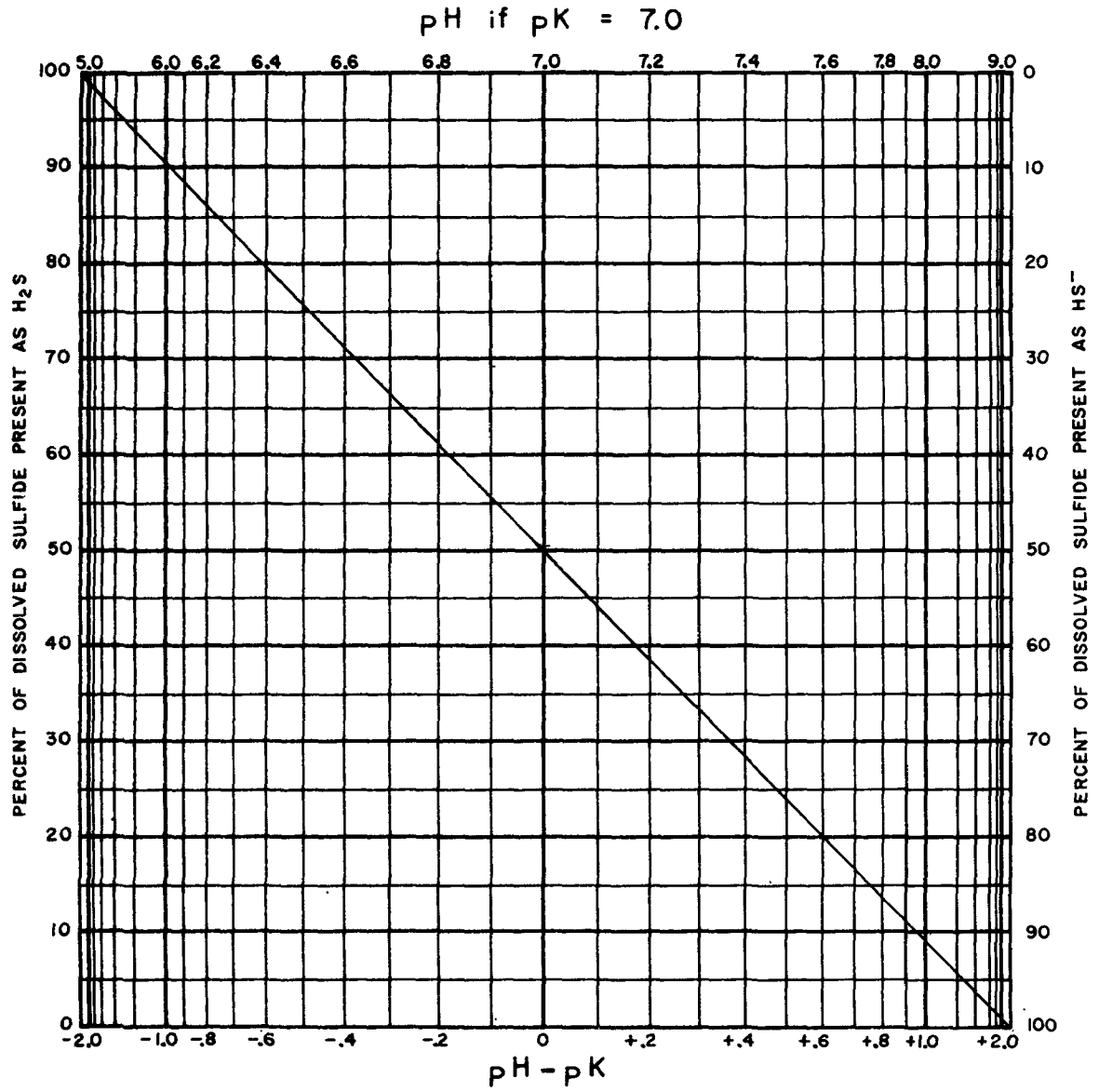
*Approximates sea water

Table 2-3 shows the proportion of dissolved sulfide existing as H_2S (a ratio indicated herein as the j factor) as a function of $pH - pK'$, or as a function of pH if $pK' = 7.0$. Figure 2-1 shows the information graphically.

The rate at which H_2S can escape from solution into the air under any given conditions of exposure is proportional to the H_2S concentration. Thus, at a pH of 7.0, H_2S will escape about half as fast as from a strongly acid solution having the same dissolved sulfide content. At pH 9.0, it will escape only 1 percent as fast as from an acid solution. If part of the H_2S escapes, the remaining dissolved sulfide will be divided between HS^- and H_2S in the same ratio as before, because the equilibrium re-establishes itself almost instantly.

FIGURE 2-1

PROPORTIONS OF H_2S AND HS^- IN DISSOLVED SULFIDE



higher

TABLE 2-3

PROPORTIONS OF DISSOLVED SULFIDE PRESENT AS H_2S (j Factors)

$\text{pH} - \text{pK}$	pH if $\text{pK} = 7.0$	Proportion of H_2S	$\text{pH} - \text{pK}$	pH if $\text{pK} = 7.0$	Proportion of H_2S
-2.0	5.0	0.99	+0.5	7.5	0.24
-1.8	5.2	0.98	+0.6	7.6	0.20
-1.6	5.4	0.975	+0.7	7.7	0.17
-1.4	5.6	0.96	+0.8	7.8	0.14
-1.2	5.8	0.94	+0.9	7.9	0.11
-1.0	6.0	0.91	+1.0	8.0	0.091
-0.9	6.1	0.89	+1.1	8.1	0.074
-0.8	6.2	0.86	+1.2	8.2	0.059
-0.7	6.3	0.83	+1.3	8.3	0.048
-0.6	6.4	0.80	+1.4	8.4	0.039
-0.5	6.5	0.76	+1.5	8.5	0.031
-0.4	6.6	0.72	+1.6	8.6	0.025
-0.3	6.7	0.67	+1.7	8.7	0.020
-0.2	6.8	0.61	+1.8	8.8	0.016
-0.1	6.9	0.56	+1.9	8.9	0.013
0.0	7.0	0.50	+2.0	9.0	0.010
+0.1	7.1	0.44	+2.5	9.5	0.003
+0.2	7.2	0.39	+3.0	10.0	0.001
+0.3	7.3	0.33			
+0.4	7.4	0.28			

2.3 Odor of H_2S

H_2S occurs naturally in "sulfur springs," and it may occur in decaying organic matter, particularly in rotten eggs. Its unpleasant odor is therefore well known. It has been shown that the threshold concentration in water for detection by humans is between 0.01 and 0.1 ng/l (0.00001 and 0.0001 mg/l) (3).

2.4 Toxicity of H_2S

Because H_2S is of such common occurrence, and causes no noticeable physiological effects when present in low concentrations, its lethal character has been largely ignored. By comparison, hydrocyanic acid, HCN , which also occurs naturally but only in very small amounts, is looked upon as a model of a deadly poison. No direct comparisons

have been made of the toxicity of H_2S and HCN , but they are certainly of the same order of magnitude. Death appears to have resulted from an H_2S concentration of 0.03 percent (300 ppm) in the air (4).

Hydrogen sulfide is treacherous, because the ability to sense it by smell is quickly lost. If a person ignores first notice of the gas, his senses will give him no further warning. If the concentration is high enough, unconsciousness will come suddenly, followed by death if there is not a prompt rescue. The deadliness of H_2S is well known in industries where it occurs, as in the petroleum industry, where high-sulfur natural gas and H_2S produced in refining operations are serious hazards. Deaths have also resulted from H_2S produced in swamps, from natural gas seeps, and from bathing in the water from hot springs in unventilated rooms. Many workmen in sewers have died from poisoning by H_2S (5).

2.5 Analytical Methods.

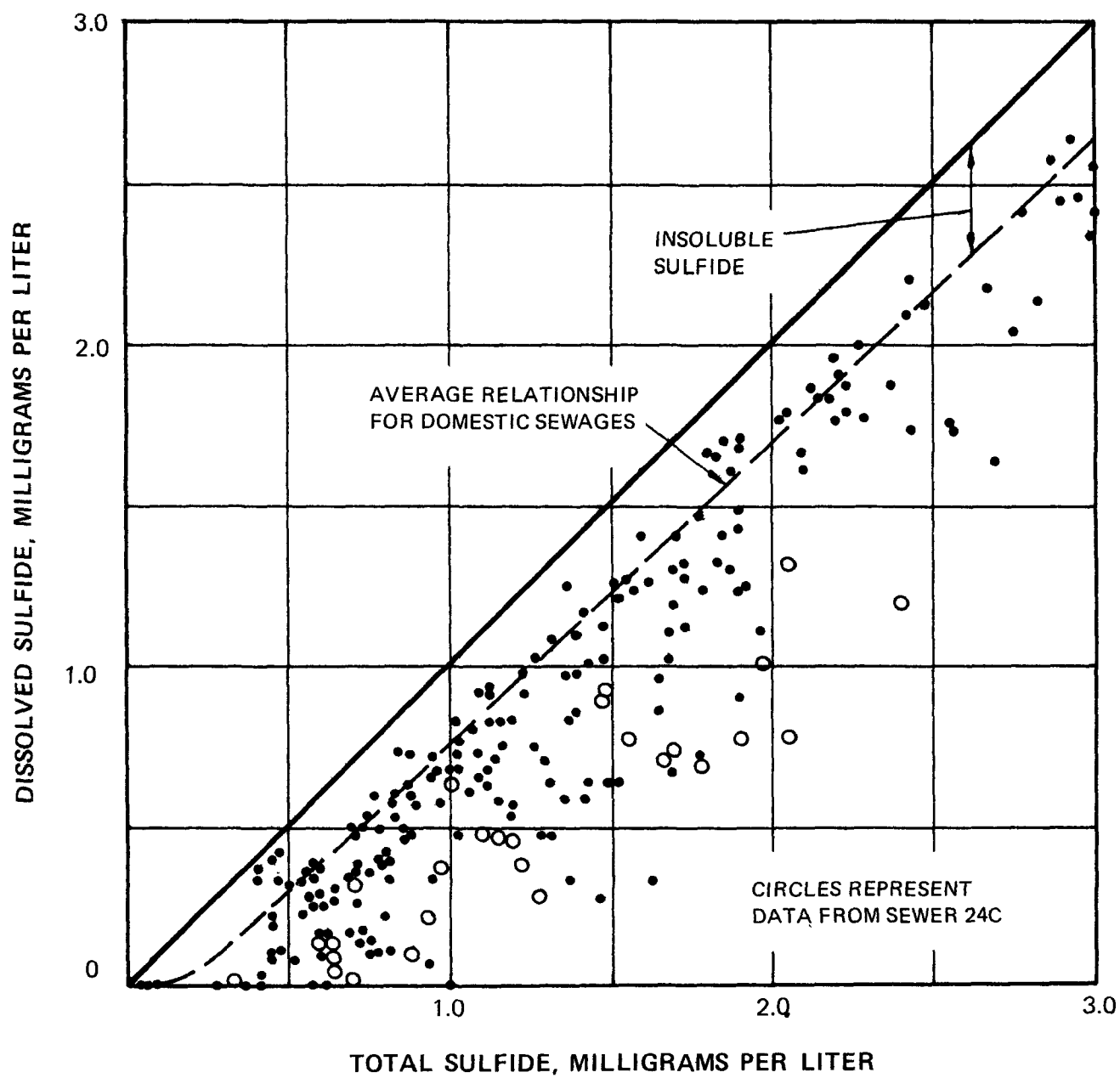
Analytically, total sulfide and dissolved sulfide must be distinguished. Dissolved sulfide is determined either by separating suspended matter with the aid of flocculating chemicals and determining sulfide in the remaining solution, or by a potentiometric titration with lead perchlorate, using an $\text{Ag}-\text{Ag}_2\text{S}$ electrode. Estimates of dissolved sulfide can also be made from the potential of the $\text{Ag}-\text{Ag}_2\text{S}$ electrode and the pH, although the results by this method are of a lower order of accuracy.

The most common sulfide test made in wastewaters is for total sulfide, using the standard methylene blue method (6). Acid is used in the test, dissolving the metallic sulfides except Cu_2S and Ag_2S , which are so inert that they are not included. When FeS_2 dissolves, only one of the two sulfur atoms appears as sulfide; the other separates as free sulfur. Three of the four sulfur atoms in Fe_3S_4 appear as sulfide. Knowledge of the dissolved sulfide content of wastewater is generally of more interest than total sulfide, but if the colorimetric test is used, it is easier to determine the total than to determine dissolved sulfide. Therefore, the total sulfide test is most often used in routine testing.

The insoluble fraction, which is the difference between total sulfide and dissolved sulfide, varies from one wastewater to another, largely in response to differences in the amounts of metals carried by the sewage. A collection of analytical data from 20 sewers in the Los Angeles County Sanitation Districts' system is shown in Figure 2-2, in which dissolved sulfide is plotted against total sulfide. In most cases, sodium sulfide had been added upstream from the sampling points in the course of research on sulfide buildup and decline. Many of the points in the figure came from wastewaters affected by metal-bearing waste, most notably the points from sewer 24C, distinguished by open circles. The dashed line represents the typical comparison of total and dissolved sulfide in domestic wastewater.

FIGURE 2-2

COMPARISON OF TOTAL AND DISSOLVED SULFIDE CONCENTRATIONS
IN TRUNK SEWERS, Na_2S HAD BEEN ADDED IN MOST CASES



It is customary, in water and wastewater technology, to express the concentrations of the various species of inorganic sulfide in terms of the sulfur content. For example, if it is reported that a water contains 5 mg/l of un-ionized H_2S , it is understood to mean that 5 mg/l of sulfur is present in the water in the form of H_2S . The actual amount of H_2S would be 5.3 mg/l.

2.6 References

1. *Handbook of Chemistry and Physics*. Cleveland, Ohio: Chemical Rubber Publishing Company (1955).
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CHAPTER 3

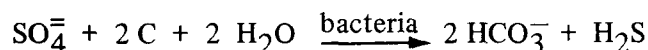
THE OCCURRENCE AND EFFECTS OF SULFIDE IN SANITARY SEWERS

3.1 The occurrence of Sulfide in Sanitary Sewers

3.1.1 Sources of Sulfide

Sulfide is sometimes present in wastewaters added to sewers, particularly in certain industrial wastes, and in rare instances groundwaters with high sulfide concentrations have leaked into sewers, but the commonest source of sulfide is biological activity in the sewer. To some extent this comes about by the decomposition of sulfur-containing organic matter, particularly the albuminoid proteins. In domestic wastewater, the major amount of sulfide results from the reduction of inorganic sulfur compounds. The word reduction is here used in its chemical sense, meaning the opposite of oxidation. An element is reduced when oxygen bonded to it is removed, or when hydrogen is added or, in general, when the valence state of the element becomes less positive.

The principal sulfur compound in wastewaters is sulfate, existing in solution as the SO_4 ion. Where organic matter is present and oxygen is absent, bacteria of the species *Desulfovibrio desulfuricans* (also called *Desulfatovacuum desulfuricans* in a recent reclassification) will reduce sulfate to sulfide, using the oxygen to oxidize organic matter. Letting C be a virtual representative of organic matter, the reaction can be written as follows:



In this reaction, 96 grams of sulfate make available 64 grams of oxygen, leaving 32 grams of sulfide. Carbon in organic matter is in a more reduced form than the free element, because of the attachment of hydrogen. An equation showing an average formula for the organic matter reacting would probably indicate that about 42 grams of organic matter would be oxidized. Sulfite, thiosulfate, free sulfur, and other inorganic sulfur compounds sometimes found in wastewaters can be similarly reduced to sulfide.

Sulfate, organic matter, and bacteria capable of bringing about the reaction that produces sulfide are present in virtually all sewers. Despite the presence of these essential elements, sulfide is not produced in all wastewater systems. In fact, severe sulfide conditions occur infrequently. A major objective of sulfide research has been to discover the reasons why sulfide appears in some sewers and not in others.

An explanation of the reasons for the observed patterns of sulfide occurrences requires an understanding of the mechanism of sulfide generation.

3.1.2 The Mechanism of Sulfide Generation

For sulfate to be reduced to sulfide requires a medium completely devoid of free oxygen or other active oxidizing agent. The stream of wastewater in a partly filled sewer is not completely anaerobic because it is exposed to the sewer atmosphere. Oxygen absorbed at the surface of the stream generally reacts quite rapidly, and in large sewers its concentration is held to a very low level, yet enough is present to prevent sulfate reduction in the stream.

The place where strictly anaerobic conditions can develop is in the slime layer that forms on the submerged pipe wall. This layer is a matrix of filamentous microbes and gelatinous material (zooglaeae) embedding various smaller bacteria. A typical slime layer may be considered to be 0.04-in thick, but if the velocity of the stream is high, it may be no more than 0.01-in thick, and if abrasive material is carried by the water, the wall may be scoured clean. At low velocities the slime may be as much as $\frac{1}{8}$ -in thick, or even more.

If oxygen is present in the stream, it diffuses into the slime layer, but the aerobic bacteria found there use it so rapidly that it advances only a very short distance. Except where oxygen concentrations are high, the aerobic zone is less than 0.01-in thick. Beneath that the slime layer is anaerobic, and it is there that sulfide generation occurs.

Calculations based upon diffusion coefficients and observed rates of sulfide production show that sulfate and/or the organic nutrients available to the sulfate-reducing bacteria are used up in a very short distance, and that the thickness of the sulfide-producing zone is generally of the order of 0.01 in. At deeper levels the slime layer is anaerobic but largely inactive because of the lack of a nutrient supply.

As long as the surface of the slime layer is aerobic, sulfide diffusing out of the anaerobic zone will be oxidized there. No sulfide will be found in the stream unless it is from some extraneous or upstream source.

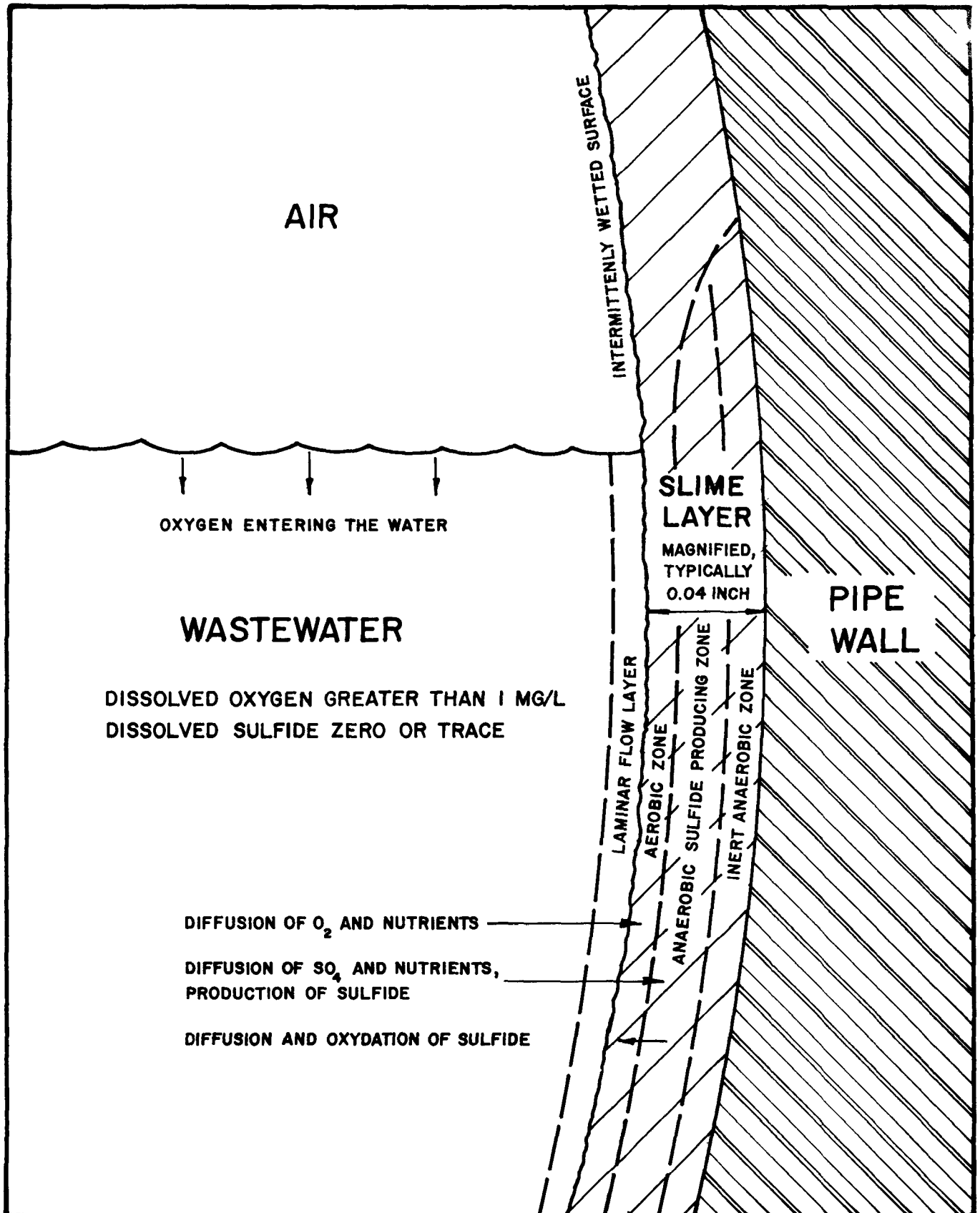
Figure 3-1 illustrates the processes just described, with the slime layer depicted on a greatly magnified scale.

It is the oxygen supply, rather than the kinds of bacteria present, that determines where the aerobic zone ends and the anaerobic zone begins. The oxygen concentration in the stream, as well as temperature and the concentration of organic food materials, determine how deep the oxygen will penetrate. If the oxygen supply increases, the aerobic zone will become thicker. Aerobes are present in the anaerobic zone, ready to oxidize the organic nutrients, but they remain dormant as long as oxygen is absent. The anaerobes, on the other hand, cannot carry on their processes as long as oxygen is present, but they are ready to resume their activity when oxygen disappears. Since these determining factors are not constant, the boundaries between the zones are not fixed. Furthermore, bits of the slime are continually sloughing off into the stream, adding to the variability of the zone boundaries.

If the oxygen concentration in the stream drops to a low level, generally a few tenths of a mg/l, not enough oxygen will reach the surface of the slime layer to oxidize all of the

FIGURE 3-1

PROCESSES OCCURRING IN SEWERS WITH SUFFICIENT OXYGEN
TO PREVENT SULFIDE FROM ENTERING THE STREAM



sulfide that is produced. Sulfide can then escape into the stream. The process is illustrated in Figure 3-2.

The oxygen concentration that is critical for preventing sulfide access to the stream is generally in the range of 0.1 to 1.0 mg/l. It depends, among other things, on temperature and on the turbulence of the stream. If the water is stationary or moving slowly, oxygen becomes depleted near the pipe wall and sulfide may escape from the slime layer even when the main bulk of the wastewater contains several milligrams per liter of oxygen. If there are organic solids slowly rolling along the bottom of the pipe, they will release sulfide even when the stream has a high oxygen content. When the oxygen concentration is low enough so that sulfide leaks into the stream, it may nevertheless be only a minor part of it that gets through. Completely anaerobic conditions must be approached before all of the sulfide produced can pass into the stream.

3.1.3 Rate of Sulfide Production by the Slime Layer

The rate at which sulfide can be produced by a slime layer is generally determined by the rate that the reactants, that is, sulfate and organic nutrients, can reach the sulfate-reducing bacteria. When the slime contains a maximum population of these bacteria and when their metabolic rate is high because of favorable temperature and other conditions, the reactants do not have far to diffuse. The rate of sulfide generation is maximal. By contrast, if the population is sparse or the metabolic rate is lower, the reactants must diffuse farther. Consequently sulfide generation is at a slower rate. If the slime layer is thin, the reactants may reach the pipe wall itself without being used up.

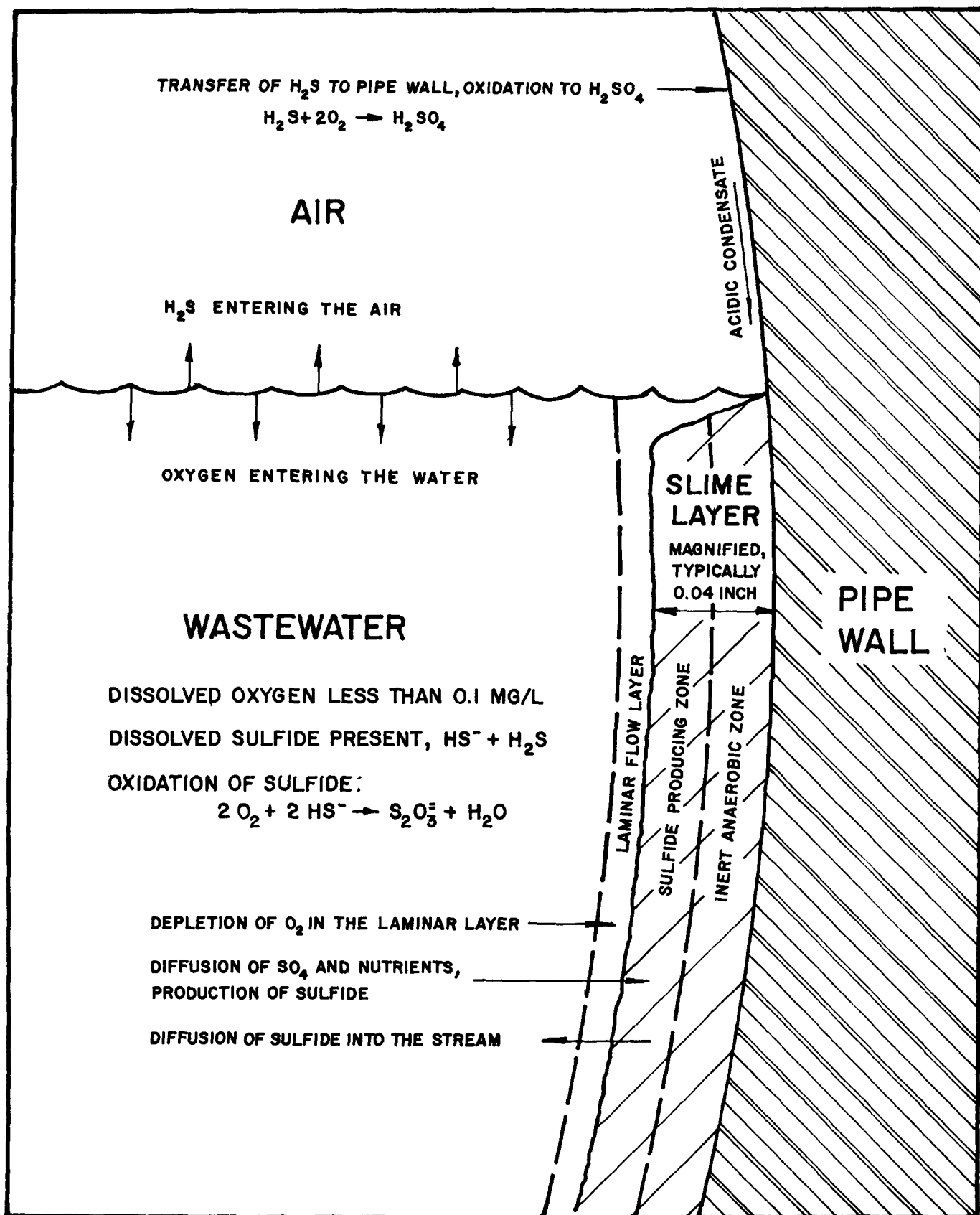
As noted in Section 3.1.1, sulfate and organic matter will be used by the sulfate reducers in a ratio of about 96 to 42. It is not likely that both will reach the reactive zone in the ideal proportions. One will be used up before the other, and the relatively scarce one will then be the constituent that limits the rate of sulfide production. If there is an abundant supply of organic matter but sulfate is scarce, then sulfide generation will be proportional to the sulfate concentration and will be independent of the amount of organic matter. On the other hand, if sulfate is abundant, the rate of generation will be proportional to the organic nutrients.

From a consideration of probable diffusion rates and relative amounts of diffusable reactants, as well as such experimental evidence as is available (1), it seems likely that the concentration at which sulfate will cease to be limiting in most wastewaters will be in the range of 20 to 100 mg/l. A range of organic materials with varying diffusion rates may be used by the sulfate-reducing bacteria, so there may be a range of conditions in which the concentrations of both sulfate and organic nutrients influence the sulfide generation rate.

A number of reports (2) have shown the oxidation of specific organic nutrients by sulfate-reducing bacteria in synthetic media, but little is known about the nutrients utilized during the production of sulfide by sewer slimes. It has been assumed (1) that these nutrients are proportional to the standard BOD in most wastewaters, and that the rate of production

FIGURE 3-2

PROCESSES OCCURRING IN SEWERS UNDER SULFIDE BUILDUP CONDITIONS



of sulfide by the slimes is proportional to the BOD if the sulfate concentration is adequate. The assumption cannot be extended to industrial wastewaters having different spectra of organic materials.

An alternative postulate (3) is that the rate of sulfide production varies as $[BOD]^{0.8}$ and as $[SO_4^{--}]^{0.4}$. It is not likely that these relationships hold when either reactant greatly over-balances the other.

The effect of temperature on the rate of sulfide production by a slime layer is complex. The increased metabolic rate of the bacteria reduces the distance that the reactants need to diffuse. At the same time, the diffusion coefficient increases. It appears that the over-all effect is about 7 percent/deg C. The term "effective BOD" has been proposed (1) as a convenient way to combine the temperature and BOD effects, as follows:

$$[EBOD] = [BOD] \times (1.07)^{(T-20)}$$

where:

$[EBOD]$ = effective BOD, mg/l

$[BOD]$ = standard BOD, mg/l

T = temperature, deg C

(1.07) = empirical factor

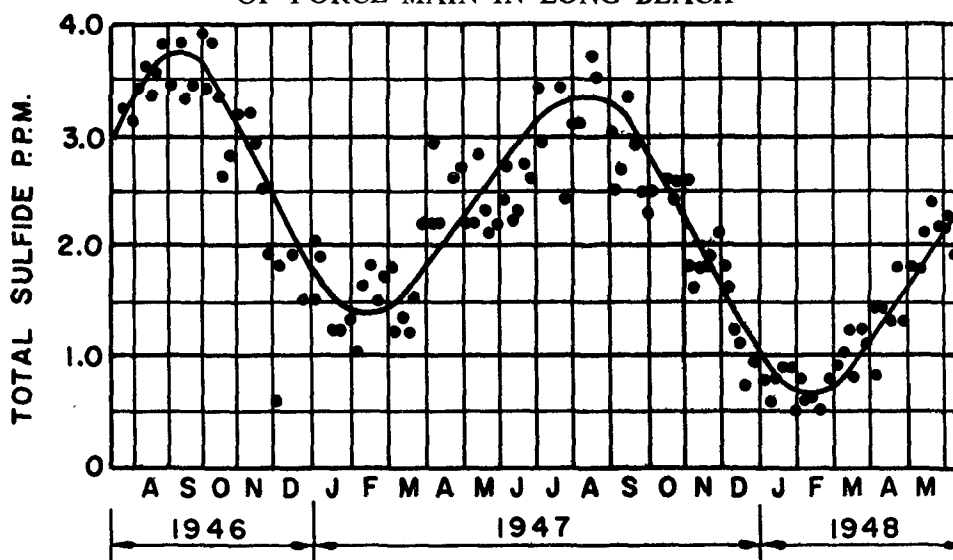
The effect of temperature on sulfide buildup is illustrated in Figure 3-3, which shows results of sulfide tests at the end of a force main that formerly transported wastewater in Long Beach, California. One test was made each week. With the array of 130 points, it is seen that there is an annual cycle, corresponding to the temperature cycle. (There is also a long-time downward trend, caused by increasing flows and consequent shorter detention time in the force main.)

There are also daily cycles resulting from patterns of flow velocities, detention times, and wastewater characteristics. In the minimum-size collecting sewers and the small trunks, sulfide generation, if it does take place, is generally not a 24-hour-a-day occurrence. During the early morning hours, when the sewage is weak, there is little likelihood of sulfide buildup in these smaller sewers.

The rate of sulfide production by a slime layer can be measured as a sulfide flux, ϕ_{se} , in units of grams/m²-hr. Assuming that the flux is proportional to the effective BOD, and that the rate is not restricted by a scarcity of sulfate, an equation can be written to define a "specific sulfide flux coefficient," M:

FIGURE 3-3

SULFIDE CONCENTRATIONS AT END
OF FORCE MAIN IN LONG BEACH



$$\phi_{se} = M [\text{EBOD}]$$

where:

$$\phi_{se} = \text{sulfide flux, g/m}^2\text{-hr}$$

$$M = \text{specific sulfide flux coefficient, m/hr}$$

$$[\text{EBOD}] = \text{effective BOD, mg/l or g/m}^3$$

The rate at which the sulfide concentration in the stream is affected by the sulfide flux from the slime layer is equal to the sulfide flux divided by the hydraulic radius. (Hydraulic radius equals one-quarter the diameter in a filled pipe.) If this is the sole source of sulfide, and if there is no oxidation or loss to the atmosphere, the following relationship holds:

$$\frac{d[S]}{dt} = 3.28 M [\text{EBOD}] r^{-1} \quad \text{(Condition: Slime layer is the sole source of sulfide, and there are no losses.)}$$

where:

$$\frac{d[S]}{dt} = \text{rate of change of sulfide concentration, mg/l-hr}$$

$$3.28 = \text{conversion factor from meters to ft}$$

$$r = \text{hydraulic radius, ft (}\frac{1}{4}\text{ the diameter in a filled pipe)}$$

Measurements in force mains and other filled pipes permit the obtaining of M values which show the maximum sulfide-producing capability of the slime layer. For the full sulfide-generating capability to be displayed, it is necessary that there be an ample sulfate concentration, no biologically inhibiting condition in the wastewater, and complete absence of oxygen. This last condition is often not met, especially at the beginning of the force main. Furthermore, the water must not be static for extended periods, because there may be local depletion of nutrients near the slime layer. Where the water is completely anaerobic, a significant amount of sulfide may be generated in the stream as well as in the slime layer.

Measurements of sulfide buildup have been made in about 40 force mains and other filled pipes. Most of the findings have been published (4) (5) (6). A correction factor was estimated for the effect of sulfide generation in the stream, and the following equation was developed:

$$\frac{d[S]}{dt} = 3.28 M [EBOD] (1 + 0.48 r) r^{-1}$$

where:

$(1 + 0.48r)$ = empirical factor for sulfide production in the stream.

This equation has been published (4), although expressed in a different way. Inherent in the form of the equation is the assumption that generation in the stream and in the slime are both proportional to EBOD.

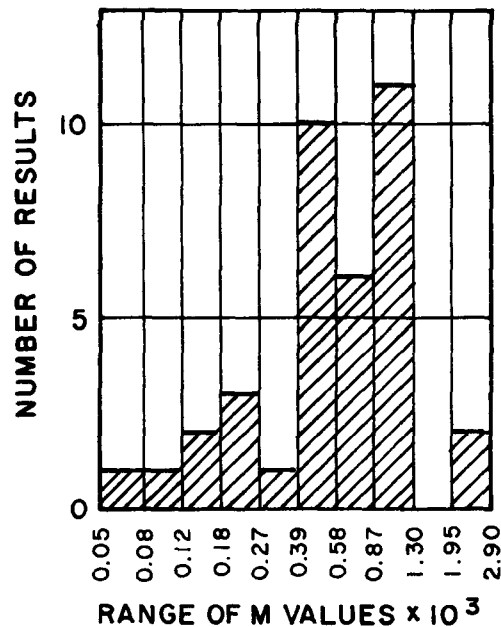
The distribution of observed values of M from the pressure main data is shown in Figure 3-4. The highest 25 percent of the results are between 0.75×10^{-3} and 1.30×10^{-3} m/hr, except for two high values found in iron pipes in which the wastewater carried a considerable percentage of seawater, and where anaerobic corrosion of iron was in progress, producing a very rough interior. It appears that $M = 1.0 \times 10^{-3}$ m/hr is a reasonable value to use for forecasting sulfide buildup in a normal force main when all conditions are favorable for sulfide buildup.

The factor most often causing low results is the presence of oxygen in the water entering the main. Sulfate deficiency, a poorly developed slime layer, or long static periods are probable reasons for low results in some cases. Sulfate concentrations are known to have been high in many of the mains where the tests were made, but actual sulfate concentrations were not recorded in most cases.

Sulfide flux coefficients have been determined in partly filled pipes by measuring sulfide buildup in the presence of enough zinc sulfate to suppress the oxidation of sulfide and to prevent its loss to the atmosphere as H_2S . Also, apparent sulfide flux coefficients have been determined by measuring sulfide buildup or decline rates in the presence of varying amounts of sulfide, and extrapolating to zero sulfide concentrations (Figure 3-10A is an example).

FIGURE 3-4

SPECIFIC SULFIDE FLUX COEFFICIENTS
FROM FILLED-PIPE DATA



However determined, values of M in partly filled sewers are generally much lower than in filled pipes. Quite commonly ϕ_{se} is zero, especially in small sewers, because there is often enough oxygen in the wastewater to prevent the slime layer from contributing any sulfide, but even where sulfide buildup in a sewer is found, ϕ_{se} is usually less than a third of what would be expected in filled pipes where oxygen is completely excluded.

Complete suppression of ϕ_{se} requires enough oxygen so that the entire slime layer has a thin aerobic zone. Because of intermittent sloughing of bits of slime and because the condition of the slime layer and the flux of oxygen to the wall vary around the submerged surface, sulfide may be released from some parts of the slime surface while it is blocked in other parts.

In very large trunks, oxygen concentrations may drop so low that ϕ_{se} may approach the values observed in filled pipes.

3.2 Gains and Losses of Oxygen in Wastewater Streams

It was shown in Section 3.1.1 that the oxygen concentration is a critical factor in determining whether the slime layer can release sulfide into the wastewater stream. For a complete understanding of sulfide buildup rates, it is necessary to examine the oxygen resources of wastewater flow in sewers.

3.2.1 Oxygen Absorption at the Surface of a Stream

One physical principle is basic to the mathematical modeling of the process of gas transfer to or from a stream of water. It may be stated thus: *The rate of approach to physical equilibrium across a phase boundary is proportional to the existing disequilibrium.* As applied to the absorption of oxygen by a stream of water, it may be stated that the flux of oxygen through a unit of surface area is proportional to the oxygen deficit, as shown by the following equation.

$$\phi_f = f D$$

where:

ϕ_f = flux of oxygen per unit area of stream surface, g/m²-hr

f = exchange coefficient, m/hr (practically the same as K_L used by some authors)

D = oxygen deficit, defined as the difference between the concentration of oxygen in the aqueous phase and the concentration that would prevail under the condition of equilibrium with the adjacent atmosphere, mg/l or g/m³

The area referred to in the definition of ϕ_f is, for practical reasons, the superficial area of water surface, or the area of a projection of an irregular interface on to a horizontal plane surface.

The validity of this equation is well established. It is valid not only for streams deficient in oxygen, but also where the stream is supersaturated, in which case the flux is in the opposite direction, and deficit is replaced by supersaturation. The relationship has been demonstrated where the supersaturation, due to photosynthesis, is at least 4 mg/l (6). Only at considerably higher degrees of supersaturation is there likely to be spontaneous bubble formation.

The following equations are useful in aeration calculations. They are either definitive or are derived mathematically from the above equation or others of the group.

The reaeration rate (R_f) is defined as the rate of change of oxygen concentration due to absorption from the atmosphere and is related to other factors by the following equation:

$$R_f = 3.28 \phi_f d_m^{-1} = 3.28 f D d_m^{-1}$$

where:

R_f = reaeration rate, mg/l-hr

3.28 = conversion factor from meters to feet

ϕ_f = flux of oxygen per unit of area, g/m²-hr

d_m = mean hydraulic depth, (defined as the cross-sectional area of the stream divided by its surface width), ft

f = exchange coefficient, m/hr

D = oxygen deficit, mg/l or g/m³

The reaeration coefficient, K_2 , is defined as the proportional rate of satisfying of the oxygen deficit. The symbol K_2 , introduced by Streeter and Phelps (7) in 1925 (but expressed in days), is equivalent to $K_L a$ as currently used by some authors, in which a is, practically, the reciprocal of d_m . K_2 is related to f and to R_f by the following equations:

$$K_2 = 3.28 f d_m^{-1}$$

and

$$R_f = K_2 D$$

where:

K_2 = reaeration coefficient, hr⁻¹

If the oxygen concentration is affected only by absorption at the surface of the stream,

$$\frac{d [O_2]}{dt} = 3.28 f D d_m^{-1}$$

where:

$\frac{d [O_2]}{dt}$ = rate of change of oxygen concentration, mg/l-hr

By integration and insertion of limits, this becomes:

$$2.303 \log \frac{D_1}{D_2} = K_2 (t_2 - t_1) \quad \text{(Restriction: surface aeration is the only factor influencing oxygen concentration)}$$

where:

2.303 = factor for conversion from log_e to log₁₀

D_1 and D_2 = initial and final oxygen deficits, mg/l

K_2 = reaeration coefficient, hr⁻¹

t_1 and t_2 = initial and final times, hr

It has been shown (8) that for the stream in a sewer, f can be reliably predicted by the equation:

$$f = 0.64 \times 0.96 C_A \Upsilon (su)^{3/8}$$

where:

f = exchange coefficient, m/hr

$0.64 = (3.28)^{-3/8} =$ conversion factor from meters to feet

$0.96 =$ empirical coefficient applicable in wastewater streams

$C_A =$ factor representing the effect of turbulence in creating additional air-water interface in comparison with a slow stream

$\Upsilon =$ temperature coefficient, equal to unity at 20 deg C

$s =$ slope of the energy line of the stream

$u =$ stream velocity, ft/sec

C_A can be approximated as shown below:

$$C_A = 1 + \frac{0.17 u^2}{gd_m}$$

where:

$0.17 =$ empirical coefficient

$g =$ gravitation constant, 32.2 ft/sec^2

$d_m =$ mean hydraulic depth, ft

(u^2/gd_m , appearing in the formula for C_A , is a Froude number; it is the square of the Froude number commonly used in the United States in respect to streams.)

It has been shown (9) that the temperature coefficient Υ varies with the turbulence of the stream. In typical sewer conditions, f increases about one percent/deg C.

Substituting the empirical equation for f into the definitive equation for R_f gives the equation:

$$R_f = 2.10 \times 0.96 C_A \Upsilon (su)^{3/8} D_m^{-1}$$

where:

R_f = reaeration rate, mg/l-hr

2.10 = $(3.28)^{5/8}$ = conversion factor from meters to feet

0.96 = empirical coefficient

On the basis of the above equations, together with calculations of required slopes to give certain velocities, Figure 3-5 has been prepared, showing reaeration coefficients in sewers of different sizes flowing half full. Also the reaeration rates are shown for the condition that the oxygen deficit is 7 mg/l, a reasonable figure to use when considering whether the oxygen supply will be sufficient to maintain a residual of 1 mg/l, to provide substantial assurance against sulfide passing from the slime layer into the stream. It should be noted that in calculating the deficit, the figure used for the solubility of oxygen should be reduced proportionally if the ambient pressure is less than one standard atmosphere and if the percentage of oxygen in the sewer atmosphere, on a dry basis, is less than the normal 20.9 percent.

Figure 3-5 is calculated for a temperature of 20 deg C. As already pointed out, an increase of temperature increases K_2 , and would correspondingly increase the rate of oxygen absorption provided the oxygen deficit remained the same. The deficit is likely to be less at higher temperature because of the lower solubility.

If the sewer flows at some depth other than half full, factors taken from Figure 3-6 can be used as multipliers for rates obtained from Figure 3-5. The velocity input when using Fig. 5 in conjunction with Fig. 6 must be the velocity that would prevail when the quantity of flow is such as to half fill the pipe, not the actual velocity for the actual quantity of flow.

3.2.2 Oxygen Absorption at Points of High Turbulence

In addition to surface aeration, oxygen is added at junctions, drops, hydraulic jumps, and other places of intensive turbulence that mixes air with the water. A simple fall or drop can be expected to satisfy a certain fraction of the oxygen deficit. It has been shown (10) that in simple falls or drops the oxygen concentration approaches saturation logarithmically with the height of the fall according to the following equation:

$$2.303 \log \frac{D_1}{D_2} = 0.305 K_H (H_1 - H_2)$$

where:

2.303 = conversion factor from \log_e to \log_{10}

FIGURE 3-5

REAERATION RATES IN SEWERS
FLOWING HALF FULL

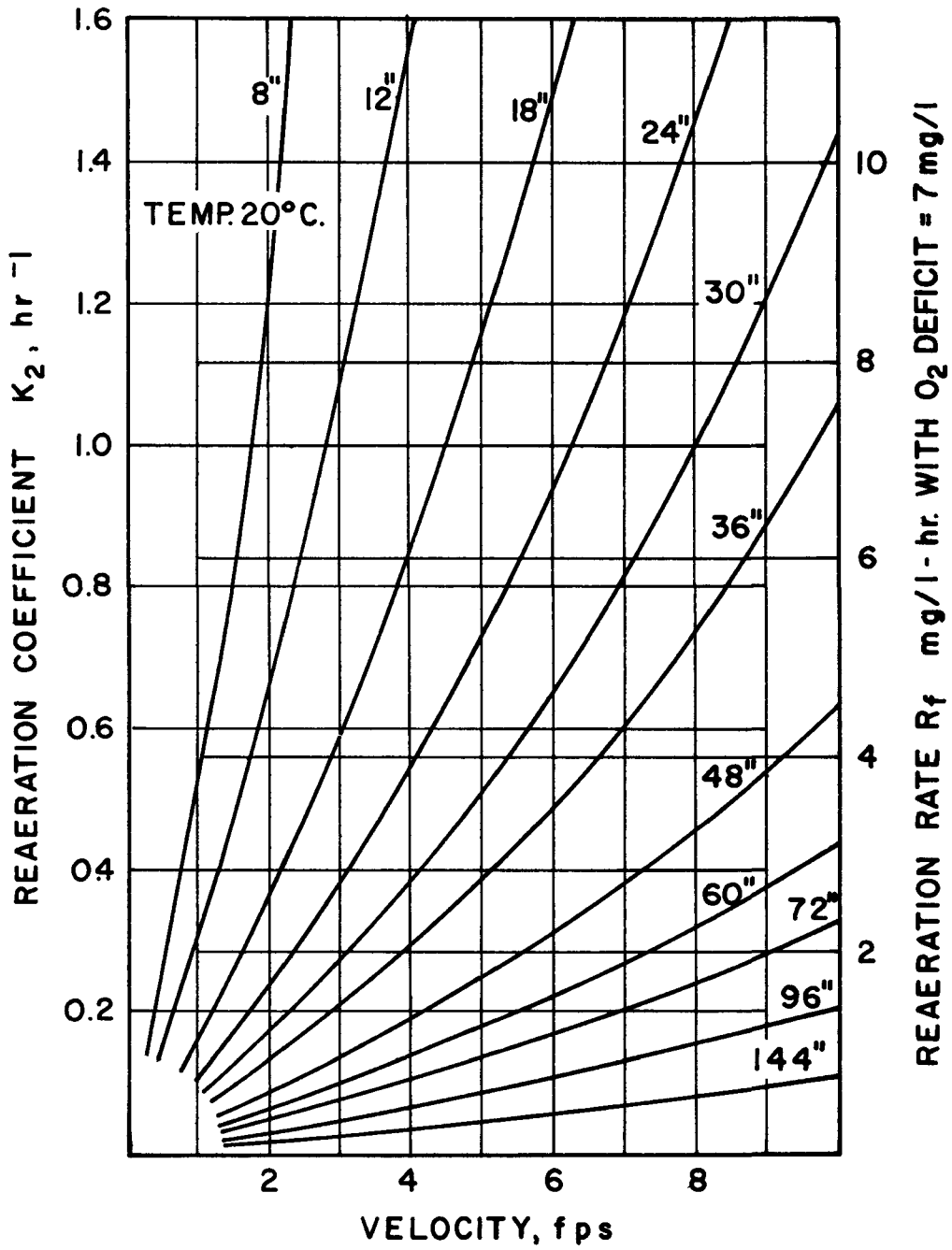
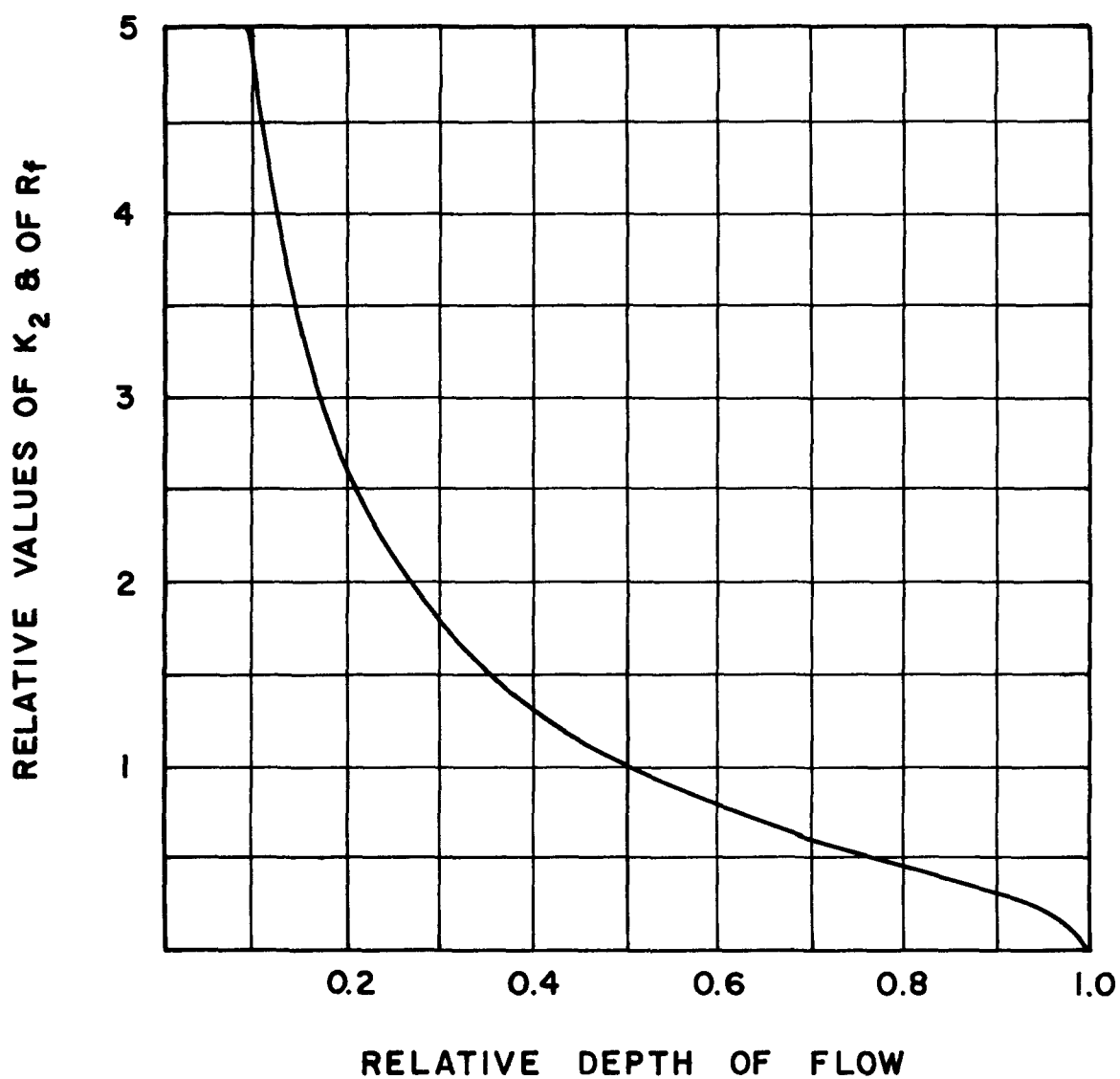


FIGURE 3-6

RELATIVE AERATION RATES IN A SEWER AT DIFFERENT FLOWS,
COMPARED TO THE RATE FOR THE HALF FILLED PIPE



D_1 and D_2 = oxygen deficits upstream and downstream from the drop, mg/l

$0.305 = (3.28)^{-1}$ = conversion factor from meters to feet

K_H = waterfall reaeration coefficient, m^{-1}

H_1 and H_2 = elevations of the hydraulic energy lines upstream and downstream from the fall, ft.

From the limited data available, it appears that an average value of K_H for wastewater is probably about $0.41 m^{-1}$. Table 3-1 shows the percentages of the deficits expected to be satisfied with various heights of fall.

TABLE 3-1
EXPECTED OXYGEN ABSORPTION IN WASTEWATER FALLS
(Tentative, Based upon $K_H = 0.41m^{-1}$)

$H_1 - H_2$	Oxygen deficit	$H_1 - H_2$	Oxygen deficit
<u>ft</u>	<u>satisfied</u>	<u>ft</u>	<u>satisfied</u>
	percent		percent
1	12	8	63
2	22	10	71
3	31	15	86.7
4	39	20	91.8
5	46	30	97.6
6	53		

In a junction where streams with different hydraulic energy lines meet, the average elevation of the energy lines above the junction and the elevation of the line for the combined flow below should be used to obtain a value of H to use in Table 3-1.

A large flow of water with a drop as little as one foot may entrain little or no air at the drop, but it may produce a hydraulic jump downstream. The efficiency of the jump in mixing air with water may not be the same as in a fall. In the absence of data, it can only be said that the hydraulic jump would probably have a similar but somewhat smaller aeration effect than a clear drop with the same energy dissipation.

It will be seen that if the stream is devoid of oxygen, so that the deficit is about 8 mg/l, a drop of 1.0 ft will result in the dissolution of about one mg/l of oxygen. This may seem like a small amount, but it could be enough to oxidize as much sulfide as would be accumulated in a mile or more of flow.

In large trunk sewers, the low slopes and the relatively deep flows cause surface reaeration rates to be very slow. A drop, however, causes approximately the same increase of oxygen concentration whether the stream is large or small. For this reason, the points of intensive turbulence are the dominant oxygen sources in large trunks.

3.2.3 Oxygen Consumption in Sewers

Short-time oxygen reaction rates in wastewaters are quite unrelated to standard BOD or even to the one-day BOD, and they change with the age of the wastewater (11).

Figure 3-7 shows equipment suitable for field use for determining oxygen concentrations in wastewater samples obtained from sewers, as well as for determinations of the oxygen reaction rates (11). For determining the reaction rate, the sample is aerated to a level of several milligrams per liter of dissolved oxygen, and then, with the disc in place, oxygen concentrations are read at suitable intervals of time.

Figure 3-8 shows results obtained with different samples of wastewater. The slopes of the lines are the oxygen reaction rates, which are preferably expressed as mg/l-hr. It is seen that the rates remain essentially constant until the oxygen concentration is below 1.0 mg/l. The slowing down of the reaction rate begins at higher oxygen concentrations in samples containing much coarse suspended matter.

Samples of sewage taken near the upper ends of small sewers show relatively low oxygen reaction rates, typically 2 to 3 mg/l-hr. The rate increases if a sample is kept aerated, and at a temperature around 20°C it may reach peak rates between 5 and 10 mg/l-hr after a few hours, after which it declines. In a sewer, the increase in the reaction rates is much faster than in bottles. This is due to the growth and shedding of biologically active material from the pipe wall. Sewage reaching the end of a metropolitan trunk has an ability to reach very high oxygen reaction rates after it is aerated for an hour or two.

Figure 3-9 shows the changing oxygen reaction rates of wastewaters from various sources when aerated in the laboratory (11). Each point on the graph represents a determination of the oxygen reaction rate as shown by the slope of the line on a plot such as those in Figure 3-8.

As wastewater moves from the small collecting sewers into the larger lines, the slopes of the sewers are in general flatter and the flow depths are greater. The effect is to decrease the rate of oxygen supply by surface aeration, but while this is happening, the rate of oxygen demand is increasing. The wastewater in small sewers is normally aerobic if the velocity is greater than 2 ft/sec. The same is true in sewers as large as 18 inches if they are flowing less than half full at a velocity of 2 ft/sec or more. In trunks 24 in or more in diameter, flowing half full at a velocity of 2 ft/sec, the oxygen concentration will usually decline to a range of a few tenths or a few hundredths of a mg/l if no oxygen is supplied other than by normal surface aeration. Oxygen consumption is then limited by oxygen impoverishment, and the rate of usage is controlled by the rate of supply.

Oxygen is used not only in the stream, but also by the slime layer. In many sewers oxygen usage by the slime layer is limited only by the rate that oxygen is transferred to the slime by the motion of the water. On the basis of somewhat limited data, a provisional equation was developed (11) to describe this oxygen flux:

FIGURE 3-7
OXYGEN MEASURING ASSEMBLY

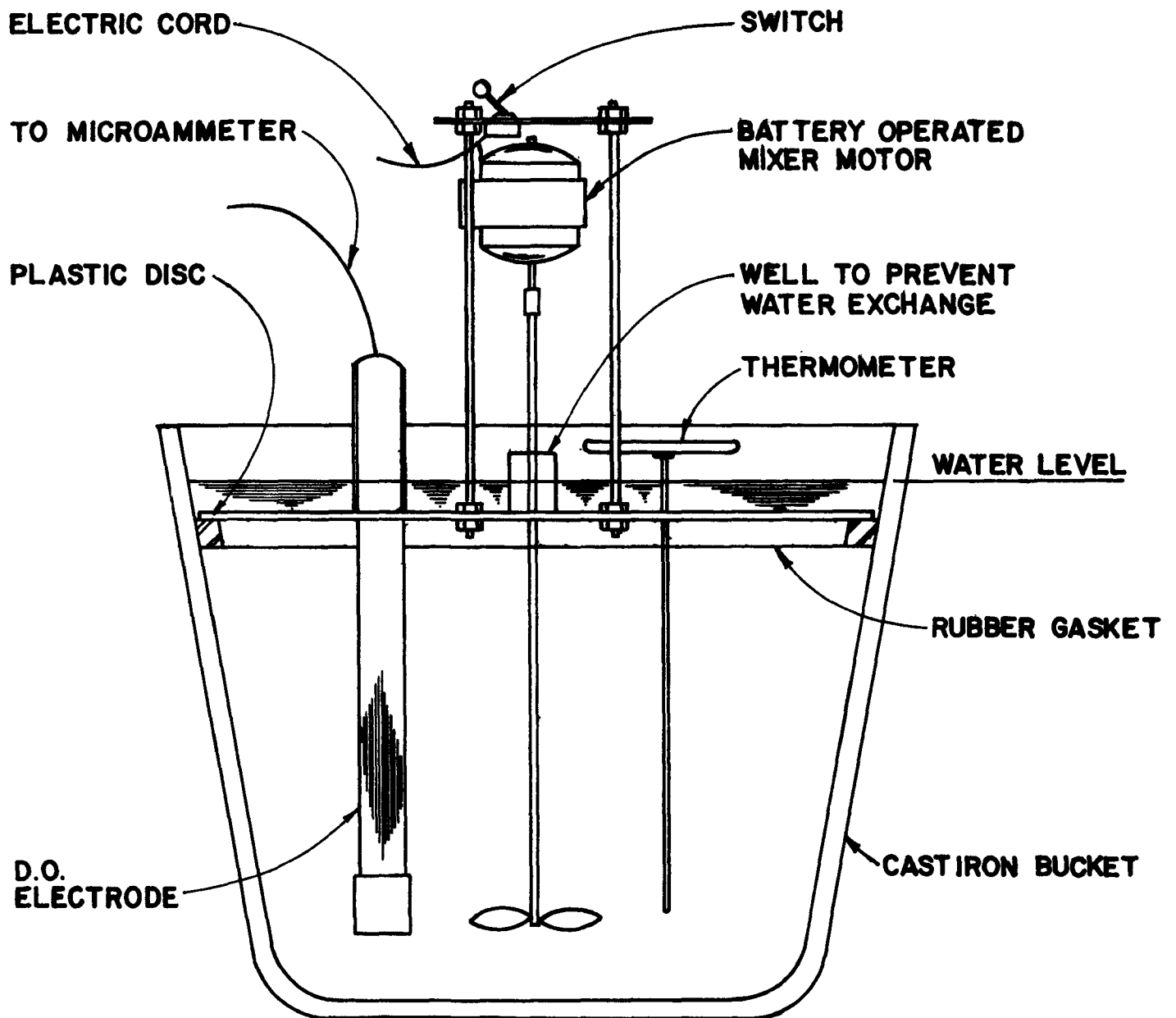


FIGURE 3-8

TYPICAL OXYGEN REACTION CURVES IN WASTEWATERS

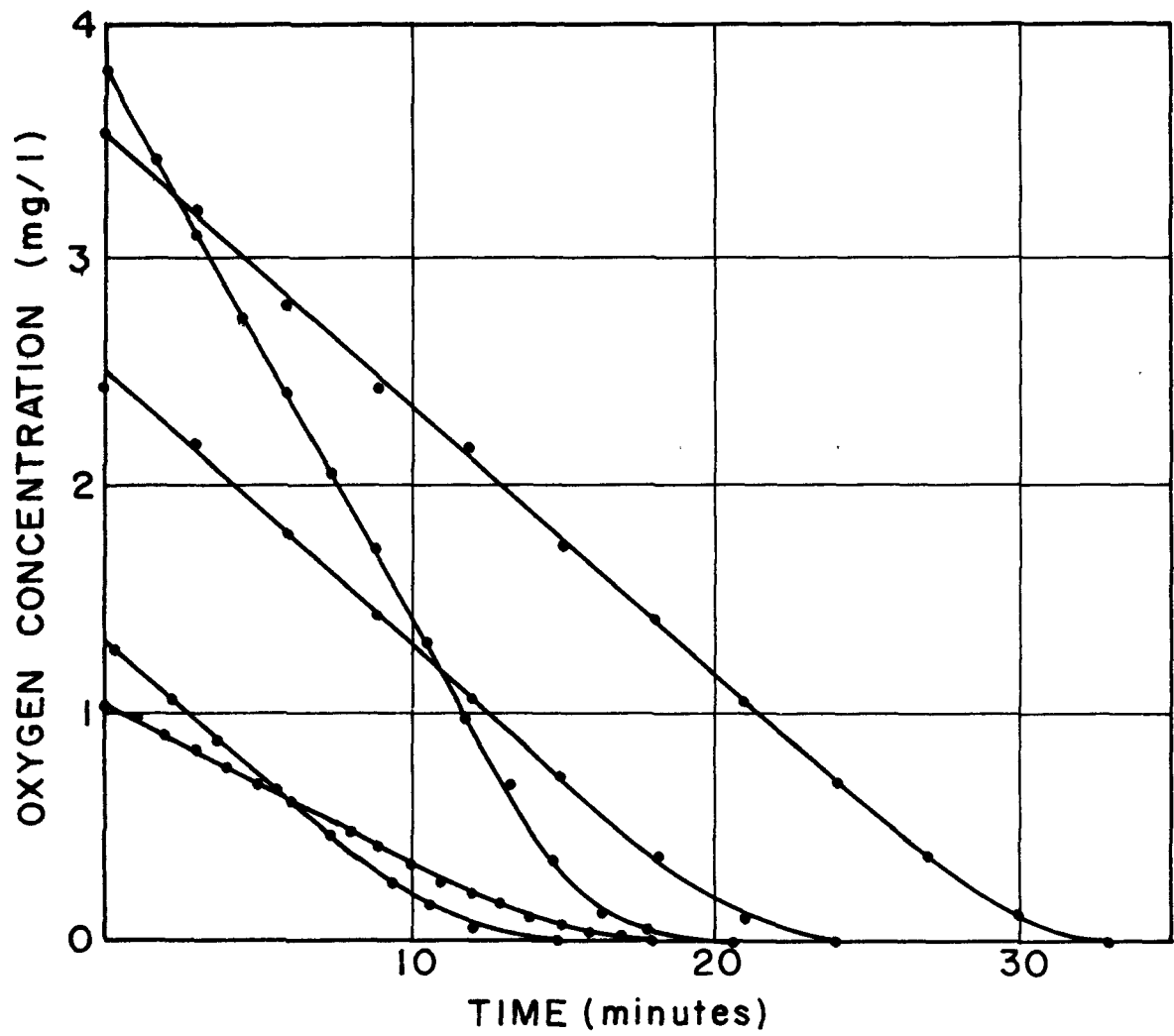
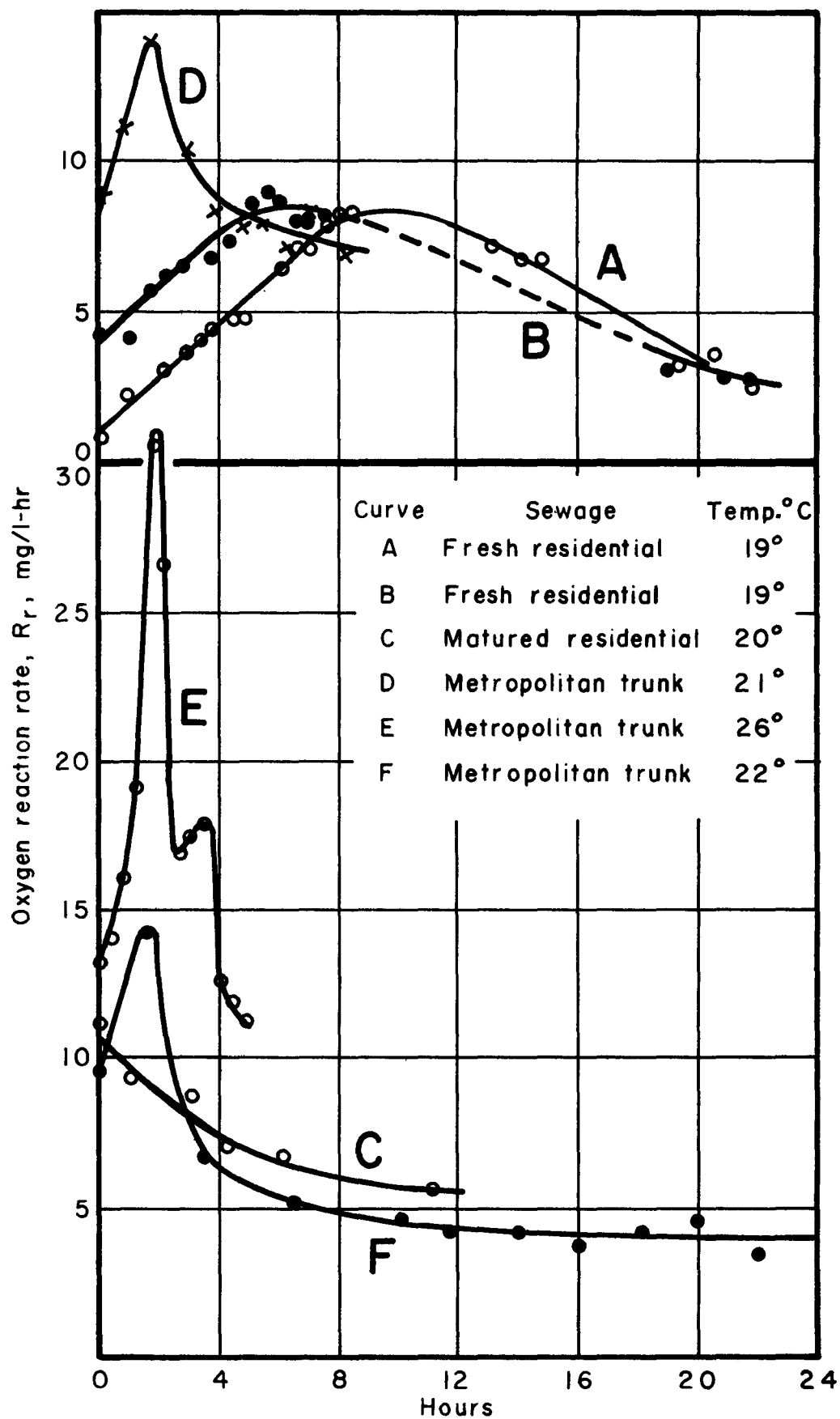


FIGURE 3-9
CHANGING OXYGEN REACTION RATES WITH TIME
IN WASTEWATER SAMPLES AERATED IN THE LABORATORY



$$\phi_e = 0.55 \times 5.3 \left[O_2 \right] (su)^{1/2}$$

where:

ϕ_e = flux of oxygen to the slime layer, g/m²-hr

0.55 = (3.28)^{-1/2} = conversion factor from meters to feet

5.3 = empirical coefficient

$[O_2]$ = oxygen concentration, mg/l

s = slope of the energy line of the stream

u = stream velocity, ft/sec

The rate of change of oxygen in the stream due to reaction at the surface of the slime layer, designated R_e , is

$$R_e = 1.78 \times 5.3 \left[O_2 \right] (su)^{1/2} r^{-1}$$

where:

R_e = loss of oxygen from the stream by reaction with the slime layer, mg/l-hr

1.78 = (3.28)^{1/2} = conversion factor from meters to ft

r = hydraulic radius of the stream, ft

In small sewers, especially where the sewage does not exhibit a rapid oxygen reaction rate and oxygen concentrations are relatively high, a major part of the oxygen usage is at the slime layer. In larger flows, oxygen concentrations are very low, the slope, s, is generally small, and the hydraulic radius of the stream, r, is large. For this combination of conditions, oxygen reaction at the surface of the slime layer is unimportant.

3.3 Losses of Sulfide

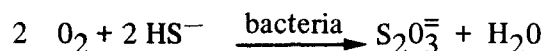
3.3.1 Reaction of Sulfide with Oxygen

Under the conditions usually found in partly filled sewers, a major part of the sulfide passing from the slime layer into the stream is subsequently destroyed by oxidation. The reaction of sulfide with oxygen may be either chemical or biochemical.

In wastewaters that are biologically inactive because of toxic substances, extremes of pH, or other reasons, sulfide is oxidized chemically. The reactions are complex, converting sulfide

to sulfate and various intermediate oxidation products. The rates vary with sulfide and oxygen concentrations, being very slow where the concentrations of either sulfide or oxygen are only a few tenths of a mg/l.

The biological reaction is more rapid. The overall product is thiosulfate, as shown below.



The weight ratio of the reactants is 0.998 part of oxygen to one part of sulfide, or, practically, 1:1. (The oxidation of sulfide to elemental sulfur, as can be brought about by *Beggiatoa alba*, does not occur to a significant extent in sewers under ordinary conditions.)

The rate of sulfide oxidation by this reaction varies with the biological activity of the wastewater, being as low as one to two mg/l-hr in fresh wastewater, but increasing to 10 to 15 mg/l-hr in wastewater that has flowed in the sewer for a few hours. The rate is independent of oxygen and sulfide concentrations as long as their concentrations are not less than 1 mg/l. The ability to biologically oxidize sulfide to thiosulfate does not appear to be confined to bacteria for which sulfide is a necessary energy source. Wastewater aerated for a few hours in the absence of sulfide and then supplied with sulfide is found to have acquired the ability to oxidize sulfide at a high rate.

In wastewater containing sulfide and one mg/l or more of dissolved oxygen, 20 percent to 30 percent of the oxygen reacting in a typical case will serve to oxidize sulfide; the rest is used by organic matter. Where the oxygen concentration is low, so that the rate of reaction is restricted by oxygen starvation, as much as 50 percent of the available oxygen may be used by the sulfide.

3.3.2 Escape of H_2S to the Atmosphere

The transfer of H_2S between a body of water and the atmosphere may be calculated from an exchange coefficient, f_s , analogous to the coefficient f for oxygen.

The exchange coefficients of different gases vary as a power of the molecular diffusion coefficients. Opinions differ as to the exponent that should be used (12) (13) (14) (15). It appears that the exchange coefficient may vary as the first power of the diffusion coefficient in a very slow stream, but that it may vary as the 0.5 power under extremely turbulent conditions. The diffusion coefficient for H_2S in water is 0.64 as great as for O_2 . Thus, the ratio of the exchange coefficients may be between 0.64 and 0.80. If an intermediate value of 0.72 is used, it is not likely to be in error by more than a few percent. Thus, from the equation for the exchange coefficient for oxygen as given in Section 3.2.1, the exchange coefficient for sulfide may be estimated as follows:

$$f_s = 0.64 \times 0.72 \times 0.96 C_A \tau (\text{su})^{3/8}$$

where:

f_s = exchange coefficient for H_2S between a stream of wastewater and a gas phase, m/hr

0.64 = $(3.28)^{-3/8}$ = conversion factor from meters to feet

0.72 = assumed ratio of exchange coefficients of H_2S and O_2

0.96 = empirical coefficient in equation for oxygen absorption in wastewater streams

C_A = factor representing the effect of turbulence in creating additional air-water interface in comparison with a slow stream

γ = temperature coefficient, equal to unity at 20 deg C

s = slope of the energy line of the stream

u = stream velocity, ft/sec

If the atmosphere were devoid of H_2S , the flux of H_2S from the stream would be the exchange coefficient multiplied by the concentration of un-ionized H_2S in the water. H_2S in the air proportionally reduces the rate of escape until it is zero when the two phases are in equilibrium. A factor, q , will be defined as the relative saturation of the air with H_2S in comparison with the equilibrium concentration. The rate of escape of H_2S is proportional to $(1 - q)$. Ordinarily the concentration of H_2S in the sewer atmosphere is between 2 percent and 20 percent of equilibrium; $1-q$ is 0.97 to 0.80. Thus, the rate of escape of H_2S is usually 97 percent to 80 percent of what it would be into a sulfide-free atmosphere.

Noting that $[H_2S] = j [DS]$; the flux of H_2S from the stream into the atmosphere is given by the equations:

$$\phi_{sf} = f_s (1-q) j [DS]$$

$$\phi_{sf} = 0.64 \times 0.69 C_A \gamma (su)^{3/8} (1-q) j [DS]$$

where:

ϕ_{sf} = flux of H_2S from the stream surface, expressed as grams of sulfide per m^2 -hr

0.69 = 0.72×0.96 from the previous equation

q = relative H_2S saturation in the air

j = H_2S factor from Table 2-3

$[DS]$ = dissolved sulfide concentration in the wastewater, mg/l

The decline of sulfide in the stream as a result of loss of H_2S to the air is equal to the flux from the surface of the stream divided by the mean hydraulic depth:

$$R_{sf} = 3.28\phi_{sf} d_m^{-1}$$

where:

R_{sf} = depletion of sulfide in the stream due to escape of H_2S , mg/l-hr

3.28 = conversion factor from meters to ft

d_m = mean hydraulic depth, ft

3.3.3 The Sulfide Balance

The rates of oxidation and of escape into the air increase as the sulfide concentration increases. Under any given set of conditions, the sulfide concentration tends to approach a limiting value at which point the losses from the stream equal the rate of supply.

To explore this relationship, rates of change of sulfide concentrations were measured in sewers to which various concentrations of sulfide were added at upstream manholes. Figure 3-10A shows the results in 24 D, a 24-in sewer at a slope of 0.0072, carrying a daytime flow averaging 3.6 cfs. Each point is the result of seven pairs of analyses at the two ends of the test reach. The points are somewhat scattered, partly because of experimental errors and partly because of variable behavior of the wastewater. With the exception of one high point, however, the trend of the points can be approximated by a straight line. It appears that in an average case during the season and time of day that the data were obtained, the initial rate of buildup of sulfide would be 0.7 mg/l-hr, and that sulfide would neither increase nor decrease if its concentration were 1.2 mg/l. Figure 3-10A is typical of results in ten sewers ranging from 10 in to 60 in in diameter (6).

From Figure 3-10A a curve has been calculated representing the buildup of sulfide that would be expected in sewer 24 D if the initial sulfide concentration were zero and if flow conditions remained uniform for a sufficiently long distance. This is shown in Figure 3-10B. If the initial sulfide concentration is not zero, the expected buildup will follow the same curve from whatever point represents the initial concentration.

3.4 Other Effects of Velocity

Up to this point, the effect of velocity has been considered only as a factor influencing the rate of absorption of oxygen and release of H_2S to the atmosphere. Velocity may also affect the thickness of the slime layer, as well as the ability of the stream to transport solids.

Observations of the effect of velocity on the slime layer are few. The slime layer varies in thickness at different locations on the submerged surfaces (16) but the minimum thickness for unimpaired sulfide generation is not known. It was shown (11) that a velocity of 7 ft/sec

FIGURE 3-10A

EFFECT OF SULFIDE CONCENTRATION
ON RATE OF SULFIDE BUILDUP OR DECLINE

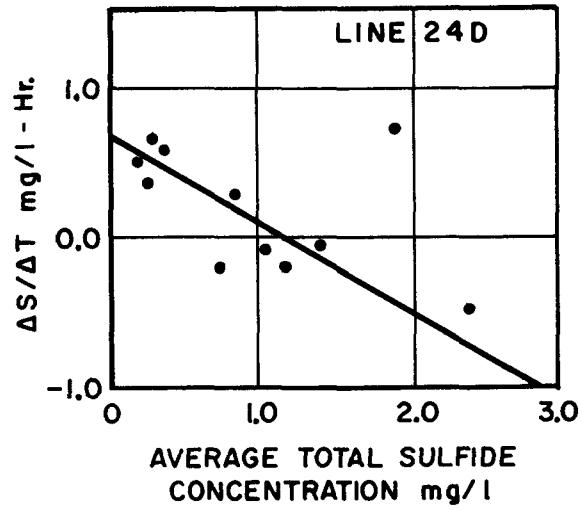
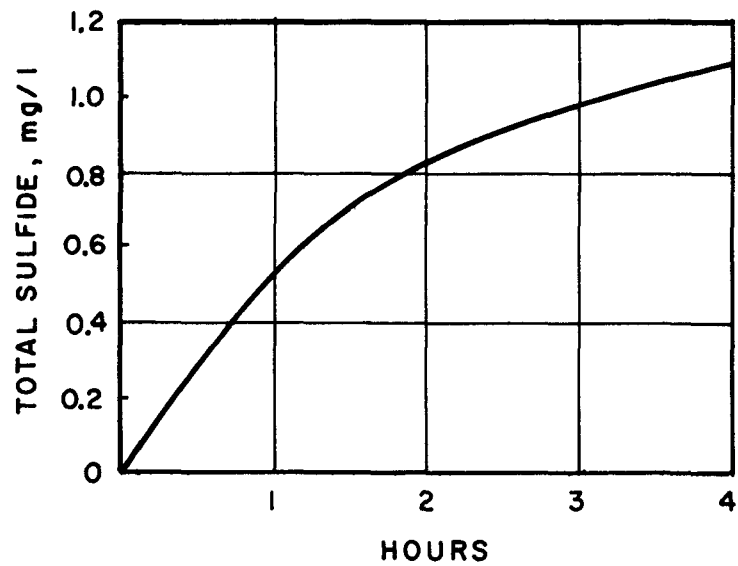


FIGURE 3-10B

SULFIDE BUILDUP CURVE, CALCULATED
FROM FIGURE 3-10 A



did not impair the ability of a slime layer to use oxygen at a maximum rate. It was also found (4) that sulfide buildup in a pressure main where the pumping velocity was 4 ft/sec was no less than in mains where the velocity was less. In view of the above work, it would not appear safe to rely upon velocity to keep the slime layer thin enough to effectively control sulfide generation. However, the slime layer may be reduced to a few mils, and at that thickness a rather small oxygen concentration might keep it aerobic or at least would prevent the small amount of sulfide that might be formed from getting into the stream.

The effect of velocity on the transport of solids is more tangible. A small amount of gritty matter lying in the pipe does not have much effect on sulfide generation, but when the velocity is slower, organic solids may concentrate at the bottom, intermittently sliding and rolling along. Because of oxygen depletion in the loosely deposited solids, and the large interfacial area, sulfide generation is then markedly accelerated. If the velocity is slow enough so that a deep, stable deposit of sludge forms, it does not proportionally increase sulfide generation, because the sludge becomes starved for sulfate, but conditions do continue to become worse with decreasing velocity. Figure 3-11 shows these relationships.

In small collecting sewers serving a few homes, velocities are generally inadequate to carry the solids in suspension. However, the stream is very shallow and the wastewater generally has a fairly high oxygen content when it enters the sewer. Sulfide buildup does not occur unless solids accumulate to a degree that causes ponding.

3.5 Forecasting Sulfide Buildup

3.5.1 Attempts at Predictative Equations

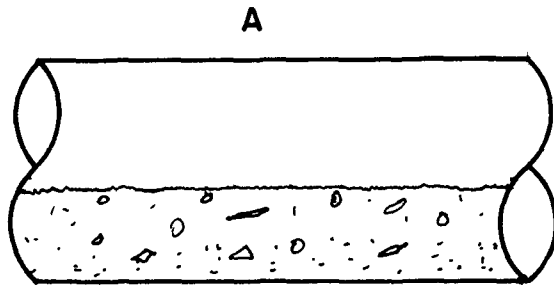
Several formulas have been proposed over a 30-year period to forecast sulfide buildup. The earlier efforts were confined to describing the marginal condition separating buildup and no buildup. The first formula published (1), expressly tentative and expressly limited to pipes not over half full, purported to define a marginal velocity above which buildup would not be expected. The marginal velocity was considered to be proportional to the square root of the effective BOD. Later the Davy equation was developed (17) which took into account the relative depth of flow, and which used a different assumption in respect to the effect of velocity on oxygen absorption.

Subsequently, the Davy equation was modified and combined with a hydraulic equation to produce what came to be known as the Z formula. The Z formula was formally published in 1970 (18), with a caution as to its provisional nature. Thisthlethwayte (3) recommends the Z formula for screening purposes, and presents a complex equation for calculating buildup rates where the Z formula indicates that there may be problems. The formula is as follows:

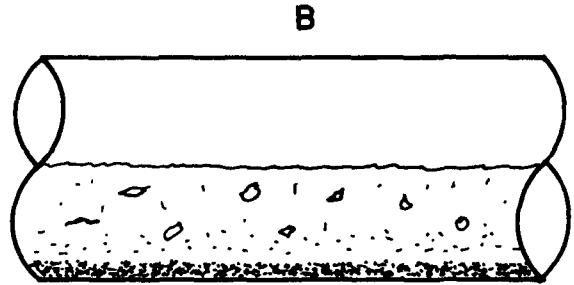
$$Z = \frac{[EBOD]}{s^{1/2} Q^{1/3}} \times (P/b)$$

FIGURE 3-11

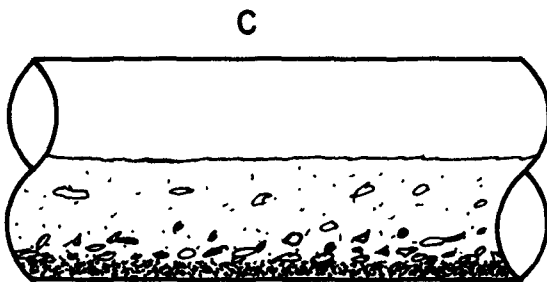
SOLIDS ACCUMULATIONS AT VARIOUS FLOW VELOCITIES



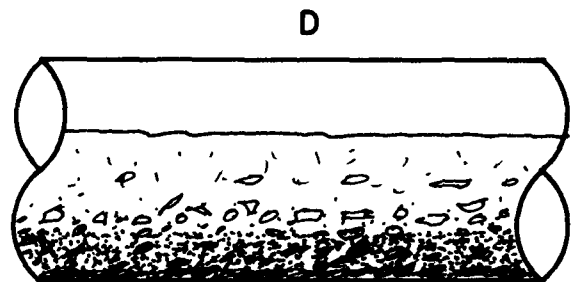
Velocity 2 fps. Efficient solids transport. No sulfide buildup in small flows, up to 2 cfs. Sulfide buildup often observed in larger flows but only at a very slow rate.



Velocity 1.4 to 2.0 fps. Inorganic grit accumulating in the bottom. More sulfide buildup as the velocity diminishes.



Velocity 1.0 to 1.4 fps. Inorganic grit in the bottom, organic solids slowly moving along the bottom. Strongly enhanced sulfide buildup; severe problems expected.



Velocity below 1.0 fps. Much organic and inorganic solid matter accumulating, overlain with slow-moving organic solids. Sulfide problems worse than in C.

where:

[EBOD] = effective BOD, mg/l or g/m³

s = slope of the energy line of the stream

Q = wastewater flow, cu ft/sec

P = wetted perimeter, ft

b = surface width, ft

Sulfide buildup is common in sewers where Z exceeds 10,000, but is rare where Z is below 5,000.

Although these equations were sometimes based upon unverified assumption, they have, in fact, been remarkably successful. Serious sulfide problems have been avoided where any one of the earlier formulas was followed in sewer design. It is now known, however, that sulfide buildup frequently does occur at a slow rate in large trunks where the predictive formulas indicate that it would not be expected, and they indicate that sulfide buildup would occur in very small flows where in fact it does not occur.

On the basis of the more adequate understanding of the sulfide generation and oxidation processes gained through researches in Australia and the United States in recent years, it is theoretically possible to write an equation that will predict the rate of change of sulfide concentration in a sewer. It could not be done on the basis of conditions in a given reach. It would be necessary to describe the history of the wastewater for 2 to 3 hours before it arrived at that reach, so that sulfide and oxygen concentrations entering the reach could be estimated. It appears impractical in any ordinary case, even though theoretically possible, to obtain all of the necessary input information. An equation can be developed to show the maximum sulfide buildup rates in uniform reaches if oxygen concentrations are low and all other conditions are favorable for buildup, but such a limited equation is not useful for the practical purposes of this manual.

Sewerage systems that have severe sulfide conditions and systems that have little or none have characteristic differences that are clearly causative. Even though a complete predictive equation is not practical, the nature of the causative relationships is now well enough understood to permit the establishment of useful generalizations, as set forth in the following subsections.

3.5.2 Conditions of Sulfide Buildup in Small Sewers

The conditions existing in the small collecting sewers are highly erratic. Because of the shallow depth and the low oxygen reacting rate in the fresh wastewater, and the effects of service laterals along the way, the stream may remain free of sulfide even though the velocity is so slow that solids are deposited.

Little is known with certainty about flows in sewers serving a few homes. The flushing of a single toilet will produce a flow of about 0.035 cfs, which is more than 100 times the daily average flow from a residence. The flow from a single flush would soon level out to a slower rate in a sewer, but more than one fixture may be in use at the same time, so occasional flows of 0.035 cfs in the sewer are not rare. A reasonable estimate is that an occasional peak flow from two houses might be 0.05 cfs. Considering the observed hydraulic conditions in small sewers (19), the peak flows from one or two residences in a sewer laid at a slope of 0.006 will not produce velocities much greater than 1 ft/sec. For a part of the time the flow will be practically zero, even from several homes. At these times, the pipe surfaces and part of the deposited solids will become quite well oxidized if solids accumulations are not excessive. This condition, and the fact that the fresh wastewater contains dissolved oxygen, will preclude sulfide generation close to the wastewater sources unless solids are stranded in such amounts that they produce stagnant pools.

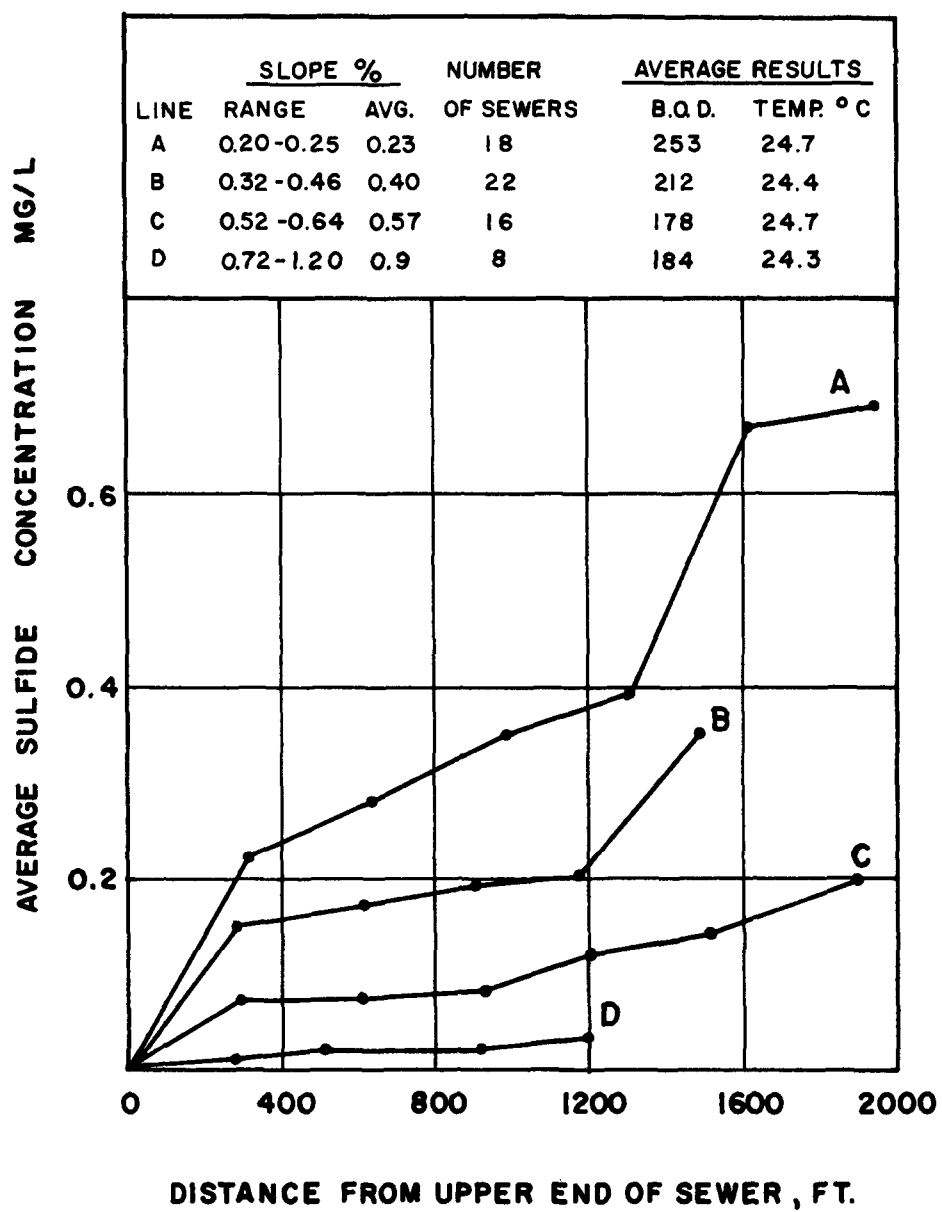
A survey of the occurrence of sulfide in small collecting sewers was made in the 1950's, largely under the sponsorship of the American Concrete Pipe Association. Sulfide analyses were made in successive manholes from the upper ends of 6-in and 8-in sewers in residential areas, continuing as far downstream as the slopes were reasonably uniform and there were no significant junctions other than service laterals. The results do not represent sulfide buildup as normally defined, because it was not a case of following the same body of sewage downstream.

The tests were made in several cities in southern California. The temperature range of the sewage was from 20 deg C to 28 deg C, with an average of 24.5 deg C. It is well known that higher temperatures cause higher sulfide concentrations, other conditions being the same, but the effects of temperature were overshadowed in this series by the effects of slope. No distinction was made between the two pipe sizes (6" and 8"), since for the same flow and slope, velocity is essentially independent of pipe size.

The sewers were divided into four slope classes, and the results averaged for each class. Figure 3-12 shows the dominant effect of slope. The increasing flows at greater distances down the sewers would eventually lead to a condition where concentrations would no longer increase, but would begin to decline. The decline would start sooner at the steeper slopes. There is not a significant indication from the data plotted in Figure 3-12 that average sulfide concentrations have passed a peak in the approximately 1,500 to 2,000-ft reaches represented by lines A, B, and C. The average housing density where the data were collected was 30 residence units per 1,000 ft of sewer. It appears, therefore, that even where the slope is 0.006 (line C), a sulfide decline will not set in until the sewer carries the wastewater from at least 60 homes (2,000 ft), and perhaps 100. Where 100 homes are served, the fluctuations of flow due to discharges from individual sources at the high-flow period of the day have been largely damped out. The peak flow is the result of the diurnal variation of average water usage. From 100 homes, a daily maximum flow rate of 0.15 to 0.20 cfs is a reasonable expectation, varying with population characteristics. The peak velocity from 100 homes in a sewer at a slope of 0.006 will probably be about 1.6 ft/sec.

FIGURE 3-12

SULFIDE OCCURRENCE IN SMALL SEWERS



The actual velocity will, of course, be less much of the time. Organic solids settle out during low flow periods, but are moved along quite well by the high flows.

For the same quantity of flow in clean pipes of circular cross section, velocity varies as the 0.41 power of the slope (19). Thus, at a slope of 0.004 (line B), the velocity in clean pipes would be 0.865 as great as at $s = 0.0057$ (line C), but because of greater fouling as the slope is diminished, the velocity would probably be even less. Because of this reduction of slope and velocity, the amount of sulfide observed is about twice as great.

There are some regions where the collecting sewers have been laid at very flat slopes, yet show no sulfide generation. This is generally because of infiltrations of groundwater, or other factors conducive to low-strength sewage and ample dissolved oxygen. The available data indicate that temperature differences are probably not a major factor in sulfide buildup in the collecting sewers.

3.5.3 Sulfide Buildup in the Larger Flows

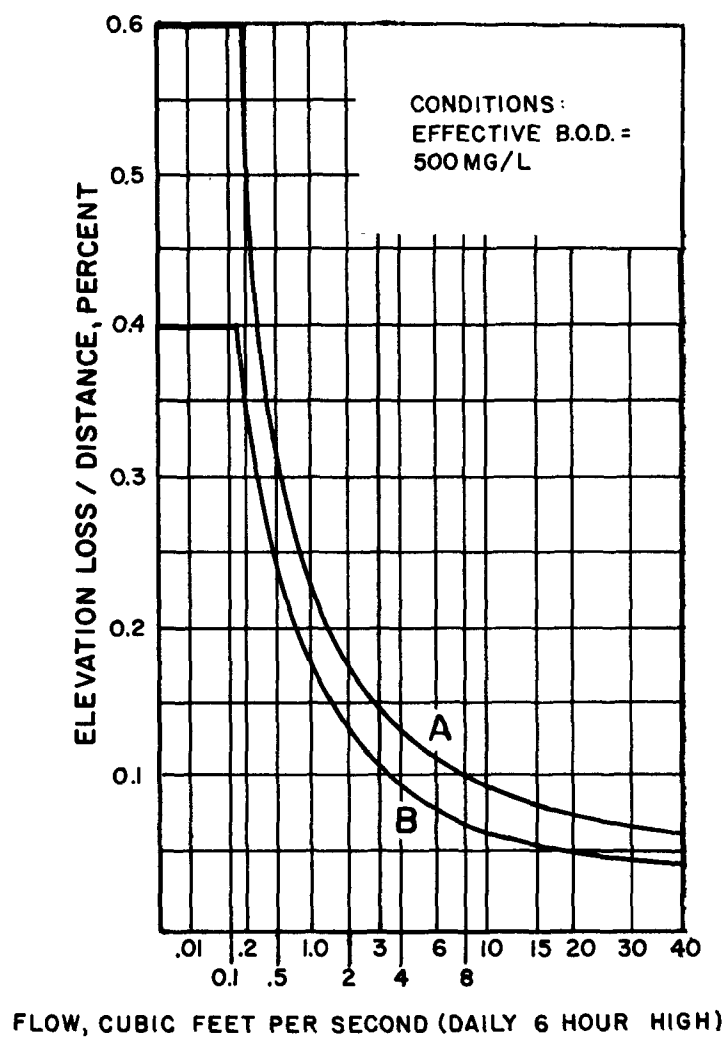
When the collected flow is great enough so that the bottom of the pipe remains essentially free of organic deposits, the determining factor in respect to the occurrence of sulfide is the oxygen balance in the stream. For flows up to one or two cfs, or more if the temperature is low, and at a velocity not less than 2 ft/sec, surface aeration is generally sufficient to maintain an oxygen residual of a few tenths of a mg/l in the stream, and to suppress sulfide buildup. In larger flows, a greater oxygen absorption rate at the surface of the stream would be necessary to prevent sulfide buildup, because of the greater volume of water that must be supplied with oxygen, but the actual absorption rate is generally less in the large sewers because of smaller slopes. However, in these larger flows the effects of junctions and other points of turbulence become more important than surface aeration of the normally flowing stream.

It has been shown that the rate of absorption of oxygen in rivers can be expressed as proportional to the rate of loss of elevation, provided a major part of the aeration occurs in falls and rapids (15). Applying the same principle to sewers, the over-all loss of elevation occurring over a distance equal to a flow time of an hour can be considered as a crude parameter of oxygen supply. It is not possible to calculate an oxygen balance in the classical sense, because oxygen concentrations in the larger sewer drop to starvation levels, where the rate of oxygen consumption is much less than it would be if ample oxygen were present. Nevertheless, the rate of energy dissipation does appear as a major factor correlating with sulfide buildup.

Based upon an evaluation of available data, Figure 3-13 has been drawn as an aid in forecasting, in a qualitative way, the possible sulfide conditions that may occur for various slope-flow combinations in sewerage systems. (As a matter of convenience, a cube-root scale is used.) The vertical scale is the over-all slope, that is, the elevation loss averaged over distances equal to one-hour flow times, except for the small collecting sewers where it

FIGURE 3-13

FLOW-SLOPE RELATIONSHIPS AS GUIDES
TO SULFIDE FORECASTING



means the actual pipe slope. All substantial tributary flows should be considered in the calculation of energy loss. Even a small tributary flow has an important effect if it drops several feet into the larger stream.

3.5.4 Interpretation of Figure 3-13

Interpretations of Figure 3-13 will be restricted to sewers with flow depths not exceeding two-thirds of the pipe diameter. This means that there cannot be any pressure mains unless measures are taken to offset their oxygen-depleting and sulfide-producing potentials. Except in small sewers, the vertical scale can be considered to be $\Delta H/\Delta L$, where H is elevation and L is distance in the same units, calculated upstream from the point of reckoning over distances representing flow times of about an hour. It will be referred to as "effective slope." In the collecting sewers of minimum size, the actual pipe slope should be used.

The interpretation of Figure 3-13 must be qualified as being related to wastewater streams of specified characteristics. The temperature of the wastewater in a sewer follows an annual cycle, BOD and quantity of flow have diurnal cycles, and flows usually have long-time trends. It is useful to define a climactic condition as the combination of the average BOD and flow for the highest six-hour flow period of the day, and the average temperature for the warmest three months of the year. Where diurnal BOD curves have not been made, it may be assumed that the BOD for the six-hr high-flow period is 1.25 times the BOD of a flow-proportioned 24-hr composite. The climactic EBOD (effective biochemical oxygen demand) is defined by the equation:

$$[\text{EBOD}]_c = [\text{BOD}]_c \times 1.07^{(T_c - 20)}$$

where:

$$[\text{EBOD}]_c = \text{climactic EBOD, mg/l}$$

$$[\text{BOD}]_c = \text{climactic BOD, mg/l}$$

$$T_c = \text{climactic temperature, deg C}$$

Let it be assumed that the climactic EBOD for a sewer is 500 mg/l. Then the interpretation of Figure 3-13 is as follows:

Curve A. While the climactic condition prevails, a system functioning with slope-flow relationships as shown by Curve A may be expected to produce very little sulfide, rarely more than 0.1 or 0.2 mg/l of dissolved sulfide. The annual average dissolved sulfide concentration is expected to be only a few hundredths of a mg/l.

Curve B. While the climactic condition prevails, a system functioning with slope-flow relationships as shown by Curve B may produce dissolved sulfide at concentrations of several tenths of a mg/l.

It must be emphasized that Figure 3-13 cannot be used to accurately *predict* sulfide conditions. The purpose is to indicate an apparent trend in the effect of flow-slope relationship on sulfide buildup. Additional data are necessary to refine and fully substantiate the indicated relationships.

If the climactic EBOD is higher or lower than 500, the positions of the curves will be altered, except that the cut-off effective slope of 0.6 percent for Curve A at small flows will remain the same, since the determining factors are hydraulic. The relationship between EBOD and required slope is complex. The nutrients available for the sulfide-generating bacteria in the slime layer are presumed to be roughly proportional to the BOD, but the oxygen requirement to prevent sulfide buildup may not increase in the same ratio. If slope, and hence velocity, is increased, the greater turbulence not only increases oxygen absorption, but also provides more effective transfer of oxygen to the slime surface. As a result, a lower oxygen concentration suffices to prevent the escape of sulfide from the slime layer into the stream. Equally important, the length of time that the wastewater spends in transit is reduced.

Considering all factors, it is judged that similar sulfide conditions will result if the effective slopes are increased or decreased in proportion to the square root of the effective BOD. Thus, Figure 3-13 shows that for the Curve A condition, a flow of 2.0 cfs requires an effective slope of 0.175 percent. If the EBOD were 600 mg/l instead of 500, the effective slope for the Curve A condition at 2.0 cfs would be

$$0.175 \text{ percent} \times \sqrt{600/500} = 0.19 \text{ percent}$$

For a system in which effective slopes are substantially higher than required by Curve A, sulfide concentrations will be negligible for practical purposes. For conditions substantially below Curve B, higher sulfide concentrations must be anticipated, generally requiring odor and corrosion control measures, or continuous treatment of the wastewater to prevent sulfide buildup.

3.6 The Effects of Sulfide in Wastewaters

3.6.1 Outline of the Effects

3.6.1.1 Odor

The obnoxious odor of H₂S escaping from manholes, pump stations, and wastewater treatment plants is the most potent objectionable characteristic of septic sewage. Chapter 2 discusses the odor potential of H₂S.

3.6.1.2 Toxicity

Many lives have been lost from H₂S poisoning in sewers. The incidence of fatal poisoning has been less in recent years, due to greater attention to safety precautions, but a deadly atmosphere will always be a hazard in some degree.

3.6.1.3 Effects on Wastewater Treatment Processes

These effects are due to sulfide in the wastewater and not to H_2S that has escaped into the air. One effect is the adverse reaction of the activated sludge process. The growth of filamentous organisms, especially *Thiothrix*, is encouraged by the presence of sulfide. The result is a poorly-settling sludge. This is not a common occurrence, and it can be overcome by prechlorination to destroy the sulfide, but if raw wastewater must be chlorinated, the chlorine demand is greatly increased by the presence of sulfide.

3.6.1.4 Corrosion of Metals and of Cement Bonded Materials

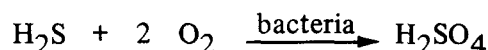
H_2S acts directly on silver and copper, first turning them black. The copper sulfide first formed oxidizes slowly, under moist conditions, to copper sulfate. Prolonged exposure causes destruction of the metal.

Cadmium is changed to yellow CdS . A similar reaction, although not properly called corrosion, is the blackening of lead-bearing paints by the formation of PbS . Iron and cement bonded materials are not directly attacked by H_2S in the air at ordinary temperatures, but they may be corroded by acid formed from H_2S . Examples are given in several publications (20) (3). The protection of existing facilities from this kind of attack, and the design of systems to avoid damage, are among the objectives of this manual. A review of the mechanism of the attack and an examination of the rate-determining factors are here presented.

3.6.2 The Corrosion of Cement Bonded Materials

3.6.2.1 The Corrosion Mechanism

The attack of cement bonded materials in the vicinity of sulfide-containing water, and in part the corrosion of iron, result from the intermediate formation of sulfuric acid by oxidation of hydrogen sulfide, as follows:



Bacteria of the genus *Thiobacillus* bring about the reaction. Under acid conditions, the functioning species is *T. concretivorus* (21). These bacteria remain active at sulfuric acid concentrations up to at least 7 percent. If the structure is made of cement bonded material, the sulfuric acid attacks the cement, producing a pasty mass of gypsum plus the residual inert materials. If the rate of production is slow, substantially all of the acid will react, but if it is formed at a rapid rate it cannot diffuse through the pasty layer as fast as it is produced, and some of it will be carried by condensed moisture back into the stream where the alkalinity of the wastewater will reconvert it to sulfate ion.

There is no over-all effect on the pH of the stream as a result of this recycling of sulfur. The production of sulfide does not lead to the corrosion of cement bonded surfaces submerged by the wastewater.

If there is no condensed moisture on the walls of the pipe or other structure, no sulfuric acid is produced. If the surface is unreactive and very high acid concentrations accumulate, sulfuric acid formation may be stopped. Under these conditions, H_2S is often oxidized to sulfur, appearing as a pale yellow deposit. If favorable conditions subsequently develop, bacteria will oxidize the sulfur to sulfuric acid.

3.6.2.2 The Distribution of Corrosion in Sewers

Corrosion of sewer pipe made of cement-bonded materials is not uniform. Lack of uniformity is due in part to the air currents that control the rate of transfer to H_2S to the pipe wall. The greatest corrosion is generally observed at the soffit of the manhole outlet, because that is where there is the greatest shear between the airstream and the pipe material. Structures projecting into the airstream suffer more rapid corrosion than the pipe wall. Test specimens hung in a sewer may provide information on the relative corrodability of different materials, but they will not show how fast a pipe wall will corrode.

There is normally a flow of air down the sewer, but in addition, transverse currents are set up by temperature differences. The pipe wall is normally cooler than the water, especially in the summer when sulfide concentrations are maximal. The air that is cooled by the walls moves downward, and slightly warmer air rises from the center of the stream surface. As a result, the maximal rate of transfer of H_2S to the pipe wall is at the crown.

Uneven distribution of corrosion also results from the migration of acid-containing condensate down the pipe wall, particularly when there is a high rate of acid production. In the zone that is intermittently washed by the water, the pasty decomposition products are cleaned away. As a result, the pipe wall is laid bare to the attack of the acid when the water level is low. Deeper penetration may therefore be observed in this zone.

Figure 3-14 shows the patterns just described, and Figure 3-15 is a photograph of a portion of a pipe showing extreme waterline corrosion, with grooves cut by the migrating acid. The pipe served in a city on the eastern seaboard of the United States. The specimen was taken near the discharge from a force main where high sulfide concentrations prevailed and where the discharge produced high turbulence.

3.6.2.3 Calculation of Corrosion Rates of Cement Bonded Pipe

The corrosion of a cement bonded sewer depends upon the supply of sulfuric acid and hence upon the rate of release of H_2S from the wastewater stream. The net mass emission of sulfur from the stream is the mass transfer to the pipe wall, except for generally negligible amounts of H_2S escaping entirely from the sewer.

Section 3.3.2 showed that the net flux of sulfide from the surface of the stream to the air can be calculated by the following equation:

FIGURE 3-14

UNEQUAL DISTRIBUTION OF CORROSION
IN A CONCRETE SEWER

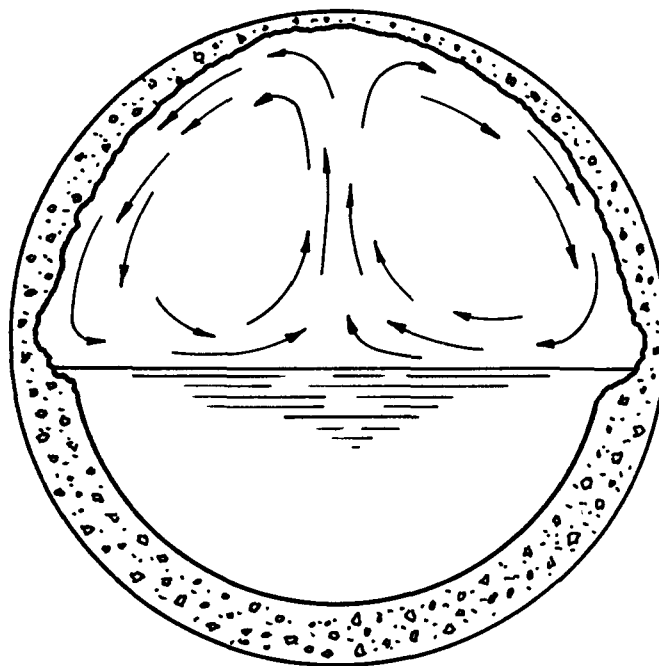


FIGURE 3-15

ACID ATTACK OF SEWER AT WATERLINE



$$\phi_{sf} = 0.64 \times 0.69 C_A \Upsilon (su)^{3/8} (1-q) j [DS]$$

where:

ϕ_{sf} = flux of H_2S (as S) from the stream to the air, g/m^2 -hr

0.64 = $(3.28)^{-3/8}$ = conversion factor from meters to feet

0.69 = empirical coefficient

C_A = factor representing the effect of turbulence in creating additional air-water interface in comparison with a slow stream

Υ = temperature coefficient, equal to unity at 20 deg C

s = slope of the energy line of the stream

u = stream velocity, ft/sec

q = relative H_2S saturation in the air

j = H_2S factor from Table 2-3

[DS] = dissolved sulfide concentration in the wastewater, mg/l

Under typical sewer conditions, excluding shallow, high velocity streams or points of high turbulence, the flux can be approximated by the following equation:

$$\phi_{sf} = 0.64 \times 0.7 (su)^{3/8} j [DS]$$

If all the escaping H_2S is oxidized on the pipe wall, the average flux to the wall is equal to the flux from the stream multiplied by the ratio of stream surface area to exposed wall area, or surface width divided by exposed perimeter:

$$\phi_{sw} = 0.64 \times 0.7 (su)^{3/8} j [DS] (b/P')$$

where:

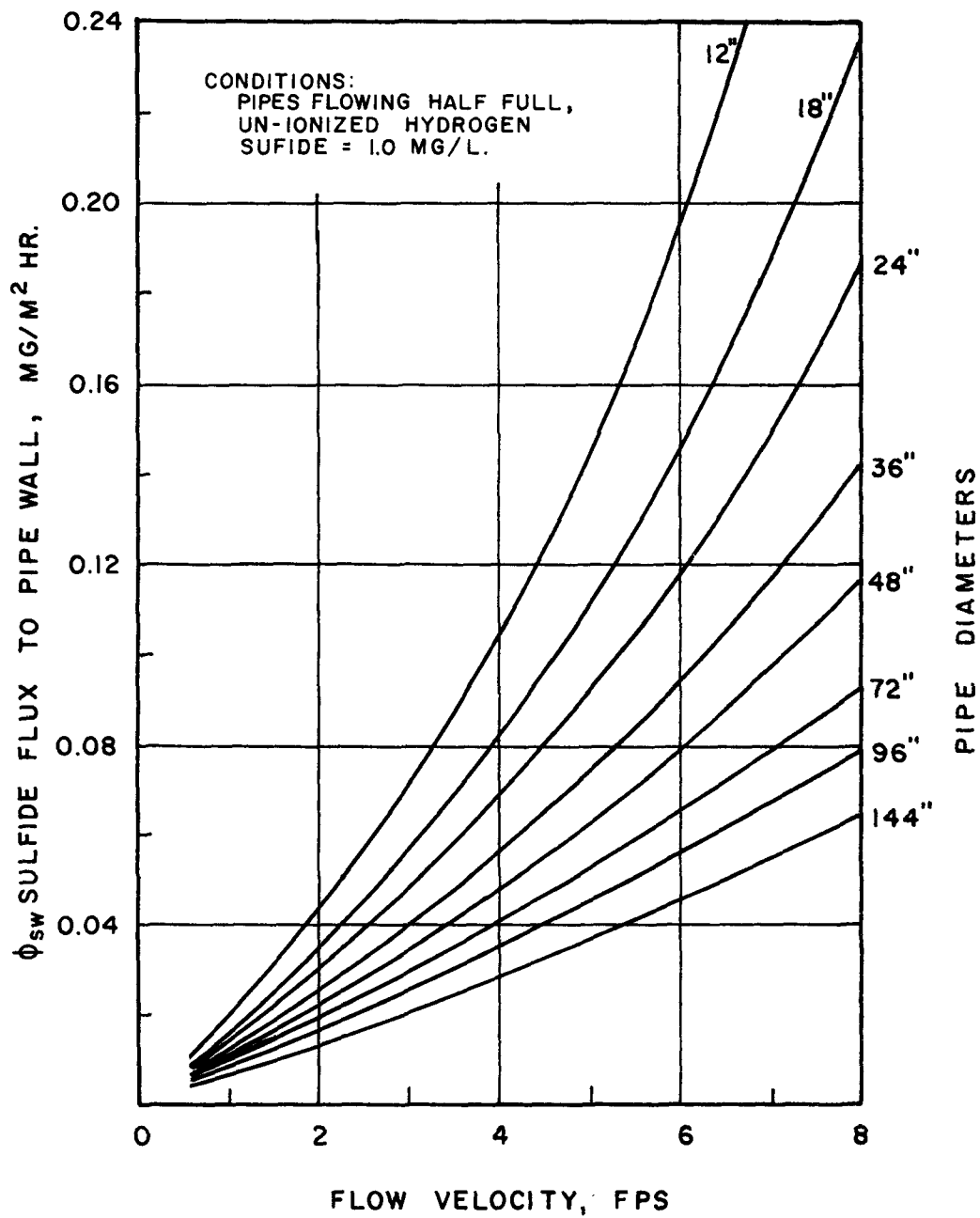
ϕ_{sw} = flux of H_2S to the pipe wall, g/m^2 -hr

(b/P') = ratio of surface width of the stream to exposed perimeter

Figure 3-16 shows rates of sulfide flux to the pipe wall in pipes flowing half full. The strong upward curvature of the curves for the smaller pipes is due to the increasing C_A factor at

FIGURE 3-16

EFFECT OF VELOCITY AND PIPE SIZE ON SULFIDE FLUX
TO PIPE WALL UNDER SPECIFIED CONDITIONS



high Froude numbers. Figure 3-17 provides factors to apply to rates from Figure 3-16 to calculate the flux at other relative flow depths. The velocity input for use in conjunction with Figures 3-16 and 3-17 must be the velocity that would prevail if the quantity of flow were such as to half fill the pipe, not the actual velocity for the actual quantity of flow.

The rate of corrosion of cement bonded material can be calculated from the amount of reactive material in the pipe wall that will consume acid, and the rate of acid production. Sulfide in the amount of 32 grams is required to produce the acid to dissolve 100 grams of CaCO_3 . If all of the acid reacts, the rate that cement bonded materials can be penetrated is as follows:

$$c' = \phi_{\text{sw}} (1/2.4) (100/32) (1/A) \times 10^{-4} = (1.3 \times 10^{-4}) (\phi_{\text{sw}}/A) \text{ cm/hr}$$

$$c' = 11.5 \phi_{\text{sw}} (1/A) \text{ mm/yr}$$

$$c' = 0.49 \phi_{\text{sw}} (1/A) \text{ in/yr}$$

where:

c' = average rate of penetration if all the acid reacts

2.4 = density of the cement bonded material

(100/32) = ratio of reacting weights of CaCO_3 and S

A = alkalinity of the cement bonded material expressed as CaCO_3 equivalent

$$10^{-4} = \text{m}^2/\text{cm}^2$$

Usually the acid does not all react, so a factor (k) must be inserted as a correction for the decrease of attack due to acid running back into the stream. The equation, therefore, may be written as follows:

$$c = 11.5 k \phi_{\text{sw}} (1/A) \text{ mm/yr}$$

$$c = 0.49 k \phi_{\text{sw}} (1/A) \text{ in/yr}$$

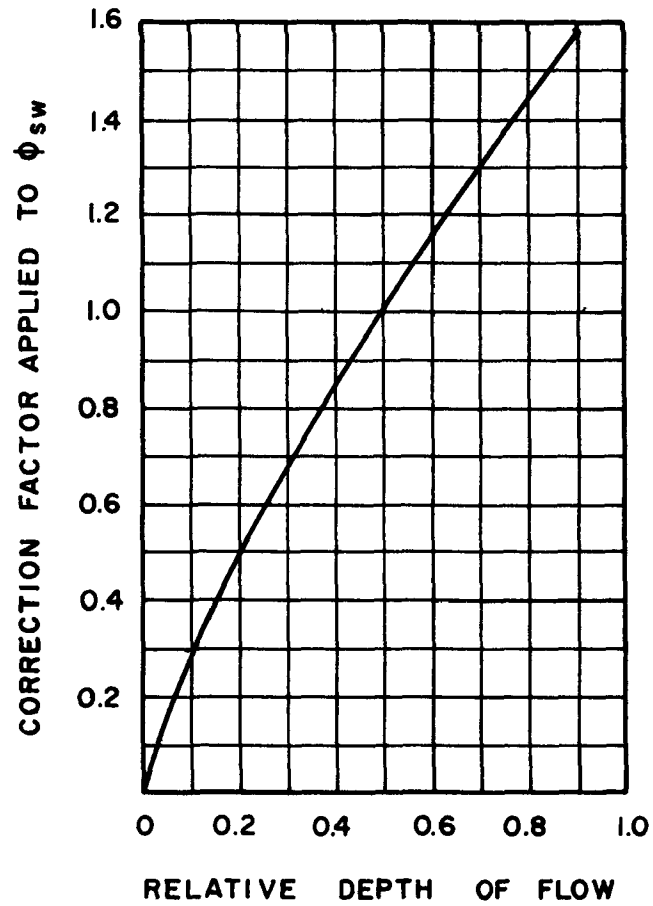
where:

c = average rate of penetration corrected for incomplete reaction of the acid

No actual measurements of k have been made, and the choice of a value to use is a matter of engineering judgment. It appears that k approaches unity when the rate of acid formation is very slow, and that it may be as low as 0.3 to 0.4 if acid production is rapid and if much condensate is formed (warm wastewater, cold pipe wall).

FIGURE 3-17

FACTOR TO APPLY TO ϕ_{sw} FROM FIG. 3-16 TO
CALCULATE ϕ_{sw} FOR OTHER THAN HALF-PIPE DEPTH

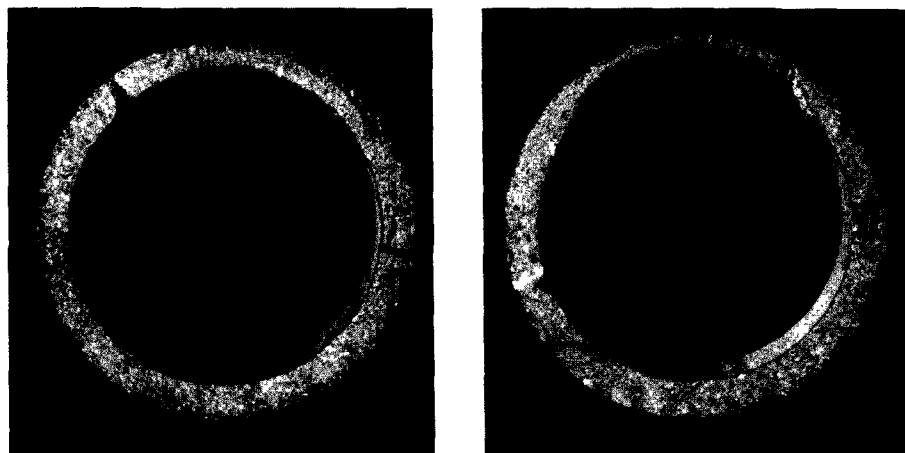


The calculation is applicable only to uniform pipe reaches well removed from points of high turbulence, and it shows only the average corrosion rate of the exposed pipe wall. It is a matter of judgment as to how much more rapid the corrosion may be at the locations of greatest penetration, which, in a uniform reach, will be at the crown or near the water line. It seems likely that the most rapid attack may be typically 1.5 times the average.

The alkalinity, A, or acid reacting capability of the pipe material, can be determined by analysis or can be estimated from the composition of the mix used in making the pipe. Anhydrous cement has an alkalinity, expressed as calcium carbonate, equal to about 1.18 times its weight. Thus, if the proportion of cement used, expressed as a percentage of the weight of the cured pipe, is multiplied by 1.18 the result is the alkalinity contributed by the cement. In concrete pipes made with granitic aggregate the alkalinity is usually between 16 and 24 percent. In asbestos cement pipe the alkalinity is usually around 50 percent.

In some areas calcareous rocks, meaning limestone or dolomite, are more available than any other hard rock, and therefore are used as aggregate for concrete. Where calcareous rocks are used in making concrete pipe, the alkalinity may be 100 percent or even higher. In many places where calcareous rock is not abundant, it has nevertheless been specified as aggregate for pipes used in sewer construction. In most of these cases a calcium carbonate equivalent of 90 percent in the finished pipe has been specified. The difference that this makes in durability under acid conditions has been repeatedly demonstrated (22) (23) (24). Figure 3-18 is a photograph of two sections of pipe that had been laid in tandem and served for 7 yr in an experimental sewer carrying high-sulfide effluent from a septic tank. (The water level was high in the pipe, so only a narrow band at the top was corroded.) The pipe marked L was made with limestone aggregate. The alkalinity of pipe L as determined by analysis was 87.9 percent; for pipe II it was 24.4 percent.

FIGURE 3-18
SECTIONS OF EXPERIMENTAL PIPES AFTER
EXPOSURE TO SEPTIC TANK EFFLUENT FOR SEVEN YEARS



CASE HISTORY

Joint Outfall B of the Los Angeles County Sanitation Districts delivers wastewater to the Joint Water Pollution Control Plant by way of a 144-in pipe installed in 1954. The line was inspected in 1974. In a carefully studied reach it was found that corrosion at the crown had penetrated the concrete to a depth of 0.25 inch. Calculations were then made by the predictive equation for the rate of corrosion.

A range of conditions needs to be considered. During a low-flow period of about 6 hr in the forenoon the flow is 150 cfs, with a depth of 6 ft and a velocity of 2.7 ft/sec. For about 6 hr in the evening it is 370 cfs, with a depth of 9.2 ft and a velocity of 4 ft/sec. From 1954 to 1963, sulfide concentrations were high due to surcharging of upstream sewers. Dissolved sulfide averaged 0.75 mg/l. With the surcharged condition largely relieved, the average dissolved sulfide concentration now averages 0.28 mg/l.

Calculations of corrosion rates were made for different combinations of conditions, but for the purpose of this example only the average condition will be used. The result in this case was very nearly the same as the average result for the conditions calculated separately.

The slope of the invert is 0.024 percent, but in the intensively studied reach the slope of the energy line ranged from 0.0131 percent to 0.0188 percent, averaging 0.0167 percent. Other input data are as follows:

Velocity, u	3.5 ft/sec
Water depth, d	8.0 ft
Dissolved sulfide, $[DS]$	0.51 mg/l
pH	7.4
pK'	6.96
j	0.275
Hydrogen sulfide, $[H_2S]$	0.14 mg/l as S
C_A	1.01
γ	1.05
$1-q$	0.97
b/P'	0.766
Alkalinity of the concrete, A	16 percent

$$\begin{aligned}
\phi_{sw} &= 0.64 \times 0.69 C_A \Upsilon (su)^{0.375} (1-q) [H_2S] (b/P') \\
&= 0.64 \times 0.69 \times 1.01 \times 1.05 \times 0.0613 \times 0.97 \times 0.14 \times 0.766 \\
&= 0.0030 \text{ g/m}^2\text{-hr} \\
c &= 0.49 \times \phi_{sw} (1/A) k \\
&= 0.49 \times 0.0030 (1/0.16) k = 0.0092 k
\end{aligned}$$

where:

c = average rate of penetration corrected for incomplete reaction of the acid

It is a reasonable estimate that the rate of acid formation at the crown of this sewer at any given time would be 1.5 times the average rate of formation on the exposed surface. It also seems likely that in this large sewer, with a moderate rate of acid formation, not more than 5 percent would be carried away from the crown by the flow of condensate, that is k is not less than 0.95. Thus, the rate of crown corrosion might be expected to be as follows:

$$c (\text{at crown}) = 0.0092 \times 1.5 \times 0.95 = 0.013 \text{ in/yr}$$

Thus, the predicted corrosion over the 20-year period would be 0.26 in. The uncertainties in the measurement of the depth of corrosion and in the input data required for the calculation could result in discrepancies that may well be as much as 40 percent of the corrosion rate. Thus, the good agreement between the observed and calculated corrosion rates, 0.0125 in/yr and 0.013 in/yr, cannot be looked upon as an indication of the precision of the predictive equation, but it does show that it is basically sound.

A major part of the corrosion in Joint Outfall B occurred in the early years when sulfide concentrations were high. The present rate of corrosion is believed to be about 0.7 in/century.

3.6.3 Corrosion Rates of Ferrous Metals

The rate of acid attack of iron and steel by acid produced by the oxidation of H_2S can probably be estimated by the same general equation as is used for cement bonded materials. For the density of iron, 7.5 would be used instead of 2.4 as for concrete, and the acid-consuming capacity, corresponding to alkalinity, would be 1.79. The equation then becomes

$$c = 0.089 \phi_{sw} k \text{ in/yr}$$

The action of acid on iron may stimulate the simultaneous reaction of the metal with oxygen, so that it is possible for the corrosion rate to be greater than would be accounted for by the acid alone.

High sulfide concentrations in water may corrode iron rapidly if oxygen is also present, producing iron sulfides, and under some conditions, especially in the presence of high chloride concentrations, iron may be corroded anaerobically with the simultaneous reduction of sulfate to sulfide (25) (26).

3.7 References

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CHAPTER 4

INVESTIGATIONS OF EXISTING SYSTEMS

4.1 Purpose

Information about sulfide conditions in existing sewerage systems is important for proper operation and maintenance, and often for the planning of new construction. An investigation may therefore be undertaken to secure this information. In addition to exploring sulfide conditions, an investigation of a system will frequently include the objective of obtaining information on carrying capacity, physical soundness, infiltration, need for cleaning, need for repairs, and sometimes an appraisal of value. Even where the objective is related only to existing or possible sulfide problems, observations should be made on the physical condition of the system, flow patterns, flow conditions as affected by solids accumulations, and characteristics of the wastewater. Often an investigation is confined to a limited part of a system, where there are known problems due to sulfide, infiltration, or poor flow conditions.

4.2 Examination of the Existing System

4.2.1 Map of the Existing System

An agency operating a sewerage system should have a map or set of maps of the sewers, showing all sewers with their sizes, slopes, types of pipe, and locations of manholes and other pertinent structures. Usually invert elevations at manholes are also shown. A city of moderate size can have all of the sewers shown on a single map, but for a large city it is necessary to have a trunk sewer map plus sectional detailed maps (1) (2). Detailed maps are necessary for whatever part of a system is the subject of an investigation, and if they do not exist, the mapping should be a part of the project.

4.2.3 Examination of Physical Conditions

The interior of all manholes in the study area should at least be viewed from the surface of the ground. Not less than 10 percent of the manholes, and sometimes 100 percent, should be entered and inspected in detail. Prior to the inspections, someone familiar with the system should locate the manholes and try the covers. In inspecting a trunk sewer, half of the time may be wasted hunting for the manholes. Sometimes they have to be dug up from beneath pavement.

When a man enters a manhole, it must be done with a full understanding of the potential hazards and in accordance with all Federal, State, and local safety regulations (3).

The conditions of the manhole, especially the steps and lower sections, should be observed and recorded. It is important to look for infiltration and to record any that is seen,

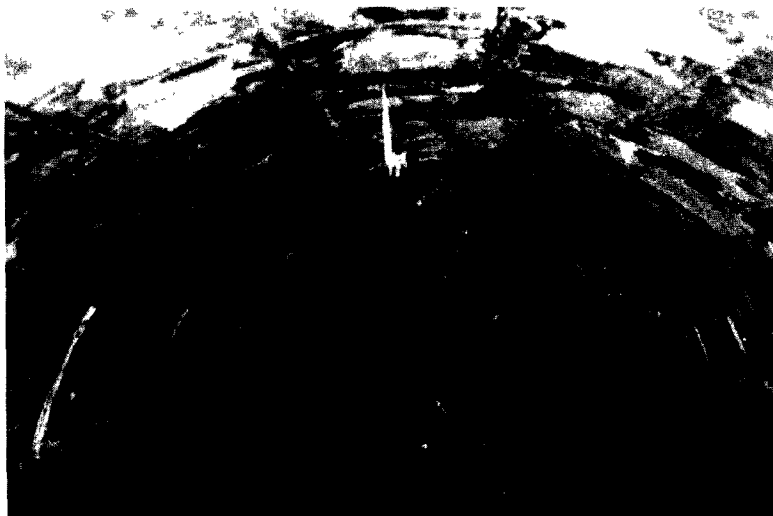
estimating or qualitatively describing the flows. The inlet and outlet pipes should be inspected insofar as possible. Two mirrors are commonly used, one held by a man at the top to reflect sunlight down the manhole, and the other used by the man at the bottom to direct the beam as well as his line of sight into the pipe. Even with reflected sunlight, the pipe cannot be effectively observed for a distance of more than 10 or 15 pipe diameters. If artificial light must be used, it should be a high-power source. Ordinary hand flashlights are not very effective.

If the pipe is corrodable, the most severe condition is generally found at the soffit, or above the soffit if the pipe is of vitrified clay or other resistant material. A condition of more severe corrosion may exist somewhere between manholes, but only if there are irregularities or junctions that cause substantially greater release of hydrogen sulfide than at the manholes. Partial stoppages are sometimes seen and can be removed at the time of the inspection.

Where it is necessary to determine the condition of the pipe between manholes, use can be made of closed-circuit TV cameras designed for the purpose. Alternatively, film cameras can be passed through the sewer, taking frequent pictures. The cost of televising or photographing is such that it is done only where it is necessary to see breaks, leaks, or other suspected abnormal conditions not visible from the manholes. Sewers to be televised generally must be cleaned first, especially if they are of the smaller sizes.

Sometimes it is necessary for men to walk through a large sewer for a detailed examination in respect to physical conditions. Sewers 45 inches in diameter and larger have been inspected in this way (Figure 4-1). Occasionally large sewers have been inspected by using a boat (4). The hazards are such that this kind of work should be done only under the direct supervision of an experienced person. Self-contained breathing apparatus is necessary unless satisfactory air conditions can be assured.

FIGURE 4-1
WALKING THROUGH
LARGE SEWER
FOR INSPECTION



4.3 Flow Measurements

Beyond visual inspection and analysis, it is frequently desirable to measure flow velocities. One way of accomplishing this is by adding some type of tracer to the wastewater. Often a dye is used. The slug of dye added should be the smallest amount that can be seen at the downstream observation point. Then averaging the "first show" and "last show" of the dye gives a close estimate of the flow time. Ideally, the first show and last show should be, for this purpose, the times that the dye concentration is 20 percent of the maximum (6). No attempt should be made to reinforce the dye to compensate for attenuation as the wastewater moves from manhole to manhole, because this leads to errors. Reflections of sunlight into the manhole will aid in seeing the dye, but observation in manholes at depths greater than 15 ft is difficult. It may be necessary under some conditions for a man to descend into the manhole to take samples or to observe the dye, or samples may be brought to the surface at frequent intervals by use of a bucket. In this case, each sample is poured into a jar. The jar with maximum color is selected, diluted with sufficient wastewater containing no dye to give 20 percent of the maximum color, and compared with the other jars to estimate the times that the dye concentration was 20 percent of maximum.

Another tracer frequently used is salt, using a conductivity meter to sense it. The downstream conductance reading should reach a peak at least twice and preferably five times the normal conductance. Radioactive tracers are also used. In this case the usual practice is to pump a stream continuously from the sewer through a counter. Any of the tracer methods will yield good determinations of velocity if properly applied.

There are several methods for measuring flow quantities. One method is velocity times cross section area of the stream. The stream in a sewer is accessible for measurement only at the manholes, which may not give reliable information as to the average condition for the whole reach. Even the averaging of measurements at several manholes might not give dependable results, because of possible consistent errors. No reliance can be placed upon such measurements where the stream is shallow. In large sewers, the errors caused by small irregularities are less important; the results, while not very accurate, may be acceptable for some purposes.

The method of greatest utility is the use of the slab type Palmer-Bowlus weir (7). This is a flat weir that yields results corresponding closely to the theoretical calculations. In comparison with a sharp-crested weir, it can measure a greater range of flows in a given sewer, and the broad crest does not collect stringy material as a sharp crest does. It is easy to install, since it is merely laid in the outlet pipe. Figure 4-2 shows one of these weirs constructed for use in an 18-in sewer. This size can be let down through the manhole opening. Larger sizes have been split longitudinally and hinged, or let down in two pieces and bolted together. It is possible to install split weirs of this type in pipes up to 36 in in diameter if it is done during the early morning low-flow period.

FIGURE 4-2
PALMER-BOWLUS SLAB-TYPE WEIR FOR 18" PIPE



Accurate measurements of flow can also be made by the dilution method. An illustration of this method is the running of a small stream of concentrated salt solution at a constant rate into the sewer, with sampling and analysis of the wastewater at a downstream location. If the chloride concentration of the salt solution and its rate of flow are known, and the increase of chloride in the wastewater above the background level is determined, the flow can be easily calculated. Lithium salts have been used for this purpose in wastewaters of high salinity since the background lithium concentration is seldom more than a few tenths of a milligram per liter.

A modification of the dilution method is to add the salt solution all at once rather than as a steady stream. Dye is added to the salt to spot the time that it passes a sampling point. The wastewater must be sampled at intervals of a few seconds. The area under the curve of concentration vs. time is used to calculate the flow. Flow and velocity are determined simultaneously. This method has been described in detail (6). Slug additions of radioactive tracers are also used to measure flows, this method being especially valuable for very large flows where it would be difficult to obtain an adequate response by use of salt.

Simple volumetric methods such as timing of the filling of the wet well of a pump station can also be used to calculate flows.

Installation of a Palmer-Bowlus weir (Fig. 4-2) in a small sewer allows the use of a stage recorder to obtain a continuous flow record. In sewers too large for the installation of weirs, the water level can be recorded, and occasional velocity and flow determinations by some other method can allow the establishment of a correlation between water level and flow. A valid correlation may not be obtainable if levels are variably affected by backup or drawdown because of hydraulic conditions downstream.

Procedures and equipment for measuring flow are discussed in detail in the Handbook for Monitoring Industrial Wastewater (5). This document should be consulted before such work is undertaken.

4.4 Character of the Wastewater

Where an investigation is made for the purpose of identifying and locating the source of high sulfide concentrations, the tests most often made include temperature, pH, total sulfide, dissolved sulfide, dissolved oxygen, BOD, COD, and oxygen reaction rate. It would not be fruitful to make all of these tests at all manholes. A reconnaissance of most of the manholes in the study area, making only sulfide tests, will aid in the selection of key manholes for more detailed study.

The diurnal cycle of sulfide concentrations must be taken into account in interpreting the results of an investigation. In a sewer where sulfide occurs, the usual pattern shows minimal amounts of sulfide at the early morning low-flow period, since this is also the time of minimal BOD. In small sewers the minimum may be zero. A rise of sulfide concentration begins after the start of the daily flow increase, generally within a half hour. After reaching a peak, sulfide concentrations usually decline somewhat to a plateau lasting, in a typical case, for six hours.

The pattern is often less distinct in very large trunks. The daily rise of sulfide concentration may lag two to three hours behind the rise of flow, because the wave of increased flow travels faster than the actual velocity of the water itself. The plateau may last eight to twelve hours. If a system contains long force mains or if sewers are subject to surcharging, the pattern may be quite different. In some systems erratic sulfide peaks may appear because of industrial waste discharges or other causes.

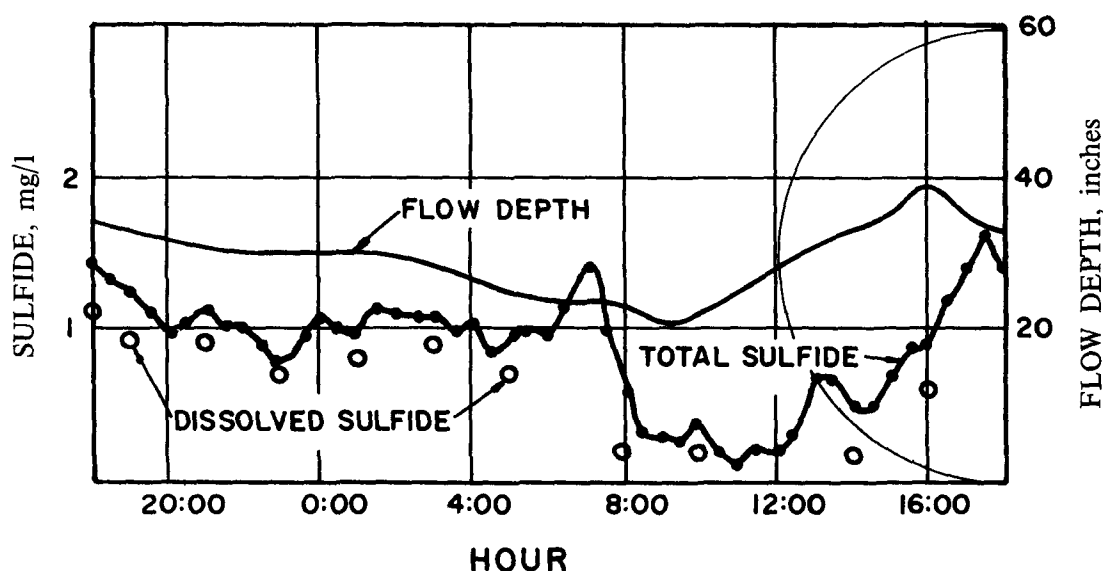
Figure 4-3 shows the results of one 24-hr test in a series of tests made in 1962 in a trunk sewer in Memphis, Tennessee, (8) illustrating some of the characteristics just described. The wastewater in this trunk occasionally showed sharp sulfide peaks that sometimes exceeded 3 mg/l, probably from an industrial source. The small peak at 7:00 in Figure 4-3 may have been from that cause.

Because of the diurnal sulfide cycle, daytime tests do not represent average conditions. However, adequate results for control purposes or for a general reconnaissance of sulfide conditions can be obtained from tests made during the sulfide plateau. An appropriate hour for routine testing can be determined from intensive testing over a period of hours, or a suitable time may be estimated from the general patterns described in the preceding paragraphs.

Instrumental methods are sometimes used for continuous monitoring of sulfide concentration. The following devices are available:

1. A simple type for measuring H_2S in air uses the principle of periodically drawing air through a strip of paper impregnated with lead acetate or other sensitive metallic salt. The strip moves after each exposure, so that if sulfide is present a row of spots is produced. The lead sulfide stain oxidizes and may fade appreciably in a few hours. A variation of this method measures the density of the color photometrically and records this result, thus eliminating the problem of fading. The results do not permit an estimate of the H_2S concentration in the wastewater, because the concentration of H_2S in air is dependent not only on the concentration in the water but also on the turbulence of the water and the turbulence of the air.

FIGURE 4-3
TYPICAL 24-HOUR SULFIDE TEST
IN A 60" INCH TRUNK SEWER



2. A modification of the first method provides for the automatic taking of samples of wastewater, which are then acidified and purged with an inert gas to transfer sulfide to the strip. Even though the method is only roughly quantitative, the results may be useful for such purposes as tracing sulfide peaks to the source.
3. H_2S removed from a sample of wastewater as in Method 2 is carried by the gas stream into a solution where it is electrolytically titrated in the presence of a bromide salt.

4. Dissolved sulfide concentrations can be calculated from automatic recordings of the potential of the Ag-Ag₂S electrode and a pH electrode. The electrodes must be cleaned and calibrated daily. The calibration is best done by making standard colorimetric determinations of dissolved sulfide in the wastewater being instrumentally monitored. The electrode system should be adjusted to give results equaling the standard method. For this method of calibration, the wastewater should have a dissolved sulfide concentration in excess of 0.5 mg/l.

After an intensive survey of a sewerage system to identify sulfide conditions, it may be concluded that there are key manholes that should be watched, especially if sulfide control procedures are being applied. These key manholes will then be sampling points for weekly or daily sulfide tests.

If there is a pressure main in the system, the operating characteristics of the pump station should be determined, and ample data should be obtained on sulfide concentrations into the wet well, at the pump discharge, and at the end of the pressure main. It is usually desirable to make at least one 24-hour test. During that test, the off and on times of the pump should be recorded. The wet well volume between high and low water should be calculated. From the data, calculations can be made of pumping rate and detention times in the pressure main. The detention time in the main can be checked by use of a dye, preferably injecting the dye solution at the pump discharge with the aid of air pressure.

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CHAPTER 5

CONTROL OF SULFIDE IN EXISTING SYSTEMS

5.1 Improving the Oxygen Balance

It is evident from the discussion presented in Chapter 3 that the supply and demand of oxygen is a major determinative factor in respect to sulfide buildup. Little or no buildup is expected if oxygen in the stream is not depleted below 1 mg/l. It is important to operate a system in a way to avoid unnecessary oxygen depletion, and measures can be taken to supplement the oxygen supply where it is inadequate. Relatively small oxygen supplements may be remarkably beneficial.

5.1.1 Avoiding Unnecessary Oxygen Depletion

Pump stations should be operated in such a way that wastewater is not backed up into the influent sewers, because any substantial amount of backing up will cause oxygen depletion and sulfide generation. If the sewer is used for flow equalization over a period of hours, severe sulfide problems may result. The wastewater is retained out of contact with the air, and because of the low velocity, organic solids slowly roll along the bottom, creating ideal conditions for sulfide generation. If inadequate pumping capacity makes surcharging unavoidable, the installation of adequate capacity should be high on the list of priorities.

Where the influent sewer to a pump station is used in part in lieu of a wet well, results may not be serious if the sewer is not completely filled at high water and if the retention time is short. Nevertheless, the condition is one to be avoided if possible. It is desirable to allow the pump to start and stop at short enough intervals to avoid backup. The frequent starting is not harmful to properly designed equipment.

The possibility of maximizing the aeration that occurs as wastewater falls into a wet well deserves consideration. This subject is discussed in Section 5.1.7 in connection with methods of supplementary aeration.

5.1.2 Injection of Compressed Air into Force Mains

5.1.2.1 Basic Concept of Air Injection, Transport and Absorption

Substantial sulfide generation must be expected if wastewater is held in a completely filled sewer for more than a half hour, or often for only a quarter of an hour. The injection of air into such a sewer at a low point, so that the air will travel upward in the pipe, is often a useful way to prevent sulfide buildup and to oxidize sulfide already present in the wastewater.

Air in a completely filled sloping sewer moves principally as large, discrete bubbles. If the sewer is nearly level, the air moves easily, the bubbles being long and flat. They produce little turbulence since little energy is dissipated, and little oxygen is dissolved. Under this

condition, the injection of air is not likely to be effective for sulfide control. If the pipe is steep, the bubbles of air are short and fat. For the same distance traveled, they must dissipate more energy; there is more turbulence, which creates new air-water interfaces and dissolves more oxygen.

The velocity of the air relative to the water is little affected by slope or rate of air injection, but increases with sewer diameter (1). An estimate of the velocity is obtainable from the following tentative equation:

$$u_a = 3.0 \times D$$

where:

u_a = velocity of the air relative to the water, ft/sec

3.0 = empirical coefficient

D = pipe diameter, ft

5.1.2.2 Basis of Design

The effect of pressure in a force main causes the rate of dissolution to increase somewhat more than in proportion to the power input because of the greater solubility of gases at high pressure. However, nitrogen is dissolved also, and when the pressure is reduced as the wastewater moves up the pipeline nitrogen comes out of solution, carrying oxygen out with it. The overall oxygen transfer efficiency does not increase very much at pressures beyond 30 psi unless the detention time of the wastewater is long enough so that there is substantial biological utilization of the oxygen before it can regassify.

The energy dissipated by air moving up an inclined filled pipe is equal to the energy of isothermal expansion of the air. The power of isothermal expansion of a gas is shown in the following equation:

$$(\text{hp})_a = 0.148 Q_a \left(\frac{P_1}{14.7} \right) \log \left(\frac{P_1 + P_2}{P_1} \right)$$

where:

$(\text{hp})_a$ = power of isothermal expansion in the compressed air stream, hp

0.148 = factor to convert \log_e to \log_{10} and cubic foot-atmospheres per minute to horsepower

Q_a = flow of air measured at ambient pressure, cfm

P_1 = ambient pressure, psi

P_2 = gage pressure at the injection point, psi

14.7 = standard atmospheric pressure, psi

When there is no flow of water, this energy is dissipated in turbulence, except for some loss of volume due to gas dissolving in the water.

The power efficiency of this method of aeration has been found to be similar to the efficiencies of other aeration methods (1). For the case where water is not moving, it may be expected that between 2 and 3 pounds of oxygen will be dissolved for each horsepower-hour of potential energy in the compressed air delivered to a force main under typical operating conditions. The efficiency will be influenced by the effect of pressure on the solubility of oxygen, and by the biological utilization of the oxygen within the force main.

There are energy losses involved in converting the electrical energy supplied to the motor to potential energy in the injected air. One of these losses is the effect of a compression process that is largely adiabatic rather than isothermal. In a typical case, with a well designed system, 30 to 40 percent of the electrical energy input appears as potential energy of isothermal expansion in the injected air.

The required potential power of the compressed air supply to provide dissolved oxygen at a rate that will equal the oxygen consuming capability of the wastewater is equal to the oxygen requirement divided by the units of oxygen supplied per unit of power, as shown below:

$$(\text{hp})_b = \frac{(62.4 \times 10^{-6}) V R_r}{2.5} \quad (\text{water column stationary})$$

where:

$(\text{hp})_b$ = potential power of the compressed air to supply the oxygen demand, hp

62.4 = density of water, lb/cu ft

10^{-6} = conversion of ppm to parts per part

V = volume of the pressure main, cu ft

R_r = oxygen reaction rate, mg/l-hr

2.5 = lb of oxygen dissolved per hp-hr in typical case

If the water is moving, the air is partly carried along by the water, and the distance that the air moves relative to the water is thereby decreased. A part of the energy of the air goes to help lift the water, causing a slight reduction in the pumping head. The amount of oxygen dissolved is proportionately decreased.

For this more general case where there is wastewater movement, the total potential power required is given by the following equations:

$$(hp)_b = \left[\frac{(62.4 \times 10^{-6}) VR_r}{2.5} \right] \left(\frac{u_a + u_w}{u_a} \right)$$

where:

u_a = velocity of the air relative to the wastewater, ft/sec

u_w = velocity of the wastewater, ft/sec

By equating $(hp)_a$ and $(hp)_b$, the following expression is obtained:

$$Q_a = \left[\frac{(17 \times 10^{-6}) VR_r}{\left(\frac{P_1}{14.7} \right) \log \left(\frac{P_1 + P_2}{P_1} \right)} \right] \left(\frac{u_a + u_w}{u_a} \right)$$

This formula is a simplified model for a rather complex process involving a number of approximations but, since it is based upon maintaining an excess of oxygen, it will generally indicate more than enough air for sulfide control. In actual practice, sulfide control is often accomplished with a half or third as much air as would be needed to fully supply the oxygen-consuming capability of the wastewater.

At pressures greater than 40 psi, the effect of pressure on the dissolution of both nitrogen and oxygen is so large that the equation is no longer useful. It may be possible to calculate the actual dissolved oxygen curve for the pipeline at various injection rates, or the required air injection rate may be determined by trial when the system is in operation.

Use of the equation requires insertion of a value for R_r . The best way to obtain a value is to make several measurements using the apparatus and procedure described in Sec. 3.2.3 or equivalent commercial apparatus. If this cannot be done, rates may be assumed using the following table as a guide.

TABLE 5-1
SUGGESTED OXYGEN REACTION RATES

Age of Wastewater	Suggested Rate, R_r (conservative)
	mg/l-hr
1 hr at 20°C or ½ hr at 30°C	5
2 hr at 20°C or 1 hr at 30°C	10
Over 3 hr at 20°C or 1½hr at 30°C	15

Special consideration must be given to situations that are out of the ordinary. For example, if most of the rise occurs in the early reaches of the pressure main, followed by a long, nearly flat run, there might be oxygen depletion and sulfide buildup in the latter portion.

In some cases, prevention of sulfide buildup may not be the only objective of air injection. In long pressure mains, substantial BOD reduction is also possible. In three force mains operating with air injection, BOD reductions of 16 mg/l (1), 60 mg/l (2), and 10 mg/l (3) have been reported.

In a very long high-pressure main, a sufficient oxygen supply to prevent sulfide generation for the entire length may result in initial oxygen concentrations that will support a fairly high rate of reaction on the slime layer. An advanced degree of biological oxidation would therefore occur by the time the end of the force main is reached. The possible reduction of BOD can be estimated, but the factors are complex and the subject is beyond the scope of this manual. If there is no premium on biological oxidation and the objective is only sulfide control, the point of air injection may be located part way up the pipeline. In one currently planned 25,000-ft force main, air will be injected at a point 8,000 ft from the discharge end.

Air injection into an existing force main may be difficult when the main has an irregular profile that could result in air blocks. In some cases it is feasible to pump against the air blocks. The total dynamic head when air is injected into a force main of irregular profile is equal to the sum of the dynamic heads of the rising legs, ignoring the descending legs, since in these legs a partly filled condition with gravity flow will prevail. (An exception should be made for a reach that has a downward slope less than the slope of the hydraulic grade line. In the calculations such a reach should be considered as part of a rising leg.) If the pumps can provide a satisfactory discharge against the sum of the dynamic heads of the rising legs, then the air blocks will not prevent a normal pumping operation.

One solution for the hydraulic problem created by an irregular profile is multiple injection points and release of air at high points. Air release valves do not operate satisfactorily in typical wastewater but an atmospheric break is often practical. In cases where this would require a standpipe of excessive height, an alternative is a continuous bleed of air and water from a high point, returning the water to a suitable point in the wastewater collecting system. Both of these methods have been used satisfactorily (2). Another alternative for accomplishing sulfide control in a force main of irregular profile is injection of air beyond the last low point, provided there is enough detention time from that point to the end of the pressure section to accomplish oxidation of sulfide produced in the unaerated portion. This plan is used in a force main serving a small residential area in Beaumont, California. The air injection point is only 300 ft from the end of the force main. In view of the short distance, the last 300 ft was made of 10-in pipe, providing a retention volume of 1,200 gal. This is twice the storage volume between high and low water in the pump station wet well, thus assuring that the contents of the aerated section will not be displaced by a single pumping.

If dissolved sulfide concentrations are not kept at zero within a force main that has a high point, with an air pocket, air injection may cause corrosion at that point. Even minor

irregularities of grade may permit the collection of pockets of air. Bubbles entering an air pocket cause turbulence that accelerates the release of hydrogen sulfide. Two pressure mains have failed because of corrosion at air pockets. Another has operated satisfactorily for 25 years with an air pocket, because the dissolved sulfide concentrations were kept low (2).

In designing air injection systems the following guidelines should be considered:

1. Continuity of treatment. The force main produces sulfide continuously, whether the wastewater is moving or static. Air injection should therefore continue whether the pump is on or off, except for short off-and-on periods to modulate the treatment.
2. Point of injection. For maximum utilization of the air, the point of injection should be at a low elevation. If there is a vertical riser from the pump, the air may be injected near the bottom of the riser, but it must be beyond the check valve and in a location where air cannot get back into the pump.
3. Manner of air injection. Air diffusers have sometimes been used. In a short distance the air collects into large bubbles, regardless of the manner of injection. If the aeration occurs mostly in a vertical riser, the diffuser may be beneficial, but in a sloping force main it is not of significant value. The usual practice is merely to pipe the air to a suitable connection into the main.
4. Choice of compressor. A major consideration is to choose a compressor suitable for long-time continuous operation with minimum maintenance. If specifications for a competitive bid for a compressor only call for equipment to compress air at a given rate to a given pressure, the low bidder is likely to supply a small, high-speed unit that will soon break down. Either minimum cylinder displacement or maximum speed should be specified. For small units the speed should not exceed 1150 rpm. For larger units the speed should be slower.
5. Provision for adjusting air rate. An air injection installation is generally designed to supply air at a rate greater than is found to be necessary in actual operation, or greater than is needed continuously. There is not ordinarily any objection to an excess of air, but for economy of operation and maintenance, provisions should be made for modifying the rate. There are several ways to do this. Often an air receiver or reservoir is used, with the air fed to the force main by way of a throttling valve and a rotameter or other flow indicator. A pressure switch either starts and stops the compressor, or, more commonly, operates a cutout that lifts the intake valves so that the compressor idles. Either method is wasteful of power. The air is over-pressurized in the receiver, and a surprising amount of energy is wasted in keeping the machinery running during the idling phase. If the size of the installation is small, the power requirement may be of little consequence, but in large units a method should be used that is less wasteful of energy. Variable

drives are a possibility. Another method is to inject air intermittently by using a program timer to start and stop the motor or to cause the compressor to idle intermittently. If the detention time for the water in the force main is long in comparison with the off-on cycle of the compressor, air bubbles will overtake water that was pumped in while the compressor was not running. Results will be similar to continuous aeration at a reduced rate. This method is used successfully in several installations of the Los Angeles County Sanitation Districts.

6. Standby. It is not customary to install standby compressors. Temporary odor control measures can be instituted if a compressor is out of service, or a portable compressor can be brought in. In large installations, however, it may be advantageous to have two compressors, one twice as large as the other. This gives a selection of three air injection rates.
7. Air flow measurement. A rotameter or other visual flow indicator should be available so that performance of the compressor can be observed. It should be installed in a bypass through which air does not normally flow.

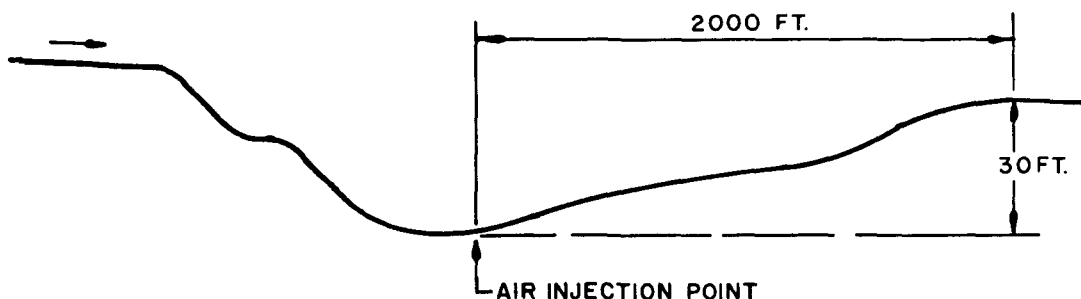
5.1.2.3 Example

Descriptions of several air injection installations have been published (1) (2), reporting, in most cases, sulfide concentrations with and without air. A hypothetical air injection design problem is presented here to illustrate the foregoing principles.

PROBLEM

An inverted siphon has a rising leg 2,000 ft long, shown schematically in Figure 5-1. It is a single 12-in pipe continuous with the sewer, and carries an average daytime flow of 1.2 cfs. The total dynamic head at the low point will be 30 ft. Daytime tests made in the summer with samples of the wastewater entering the siphon show an average oxygen reaction rate (R_r) of 11 mg/l-hr. The location is near sea level. Design a system to inject air at the low point to supply enough oxygen to meet the oxygen demand rate.

FIGURE 5-1
SCHEMATIC DRAWING OF FORCE MAIN FOR PROBLEM



SOLUTION

$$Q_a = \left[\frac{(17 \times 10^{-6}) \text{ VR}_r}{\frac{P_1}{14.7} \log \frac{P_1 + P_2}{P_1}} \right] \frac{u_a + u_w}{u_a}$$

1. Average daytime velocity of wastewater = $u_w = Q/A = \frac{1.2}{0.785} = 1.53 \text{ ft/sec}$
2. Air velocity relative to wastewater = $u_a = 3.0\sqrt{D} = 3.0\sqrt{1} = 3.0 \text{ ft/sec}$
3. $P_1 = 14.7 \text{ psi (sea level)}$
4. $P_2 = \frac{30}{2.31} = 13.0 \text{ psi}$
5. $V = \frac{\pi (D)^2}{4} (2,000) = 1,570 \text{ cu ft}$
6. $R_r = 11 \text{ mg/l-hr}$

$$Q_a = \left[\frac{(17 \times 10^{-6}) (1,570) (11)}{\frac{14.7}{14.7} \log \frac{14.7 + 13.0}{14.7}} \right] \left(\frac{3.0 + 1.53}{3.0} \right)$$

$$Q_a = 16 \text{ cfm}$$

The calculated air injection rate of 16 cfm should be enough to supply the oxygen consumption rate of the wastewater. A smaller amount often suffices to prevent sulfide buildup. To provide for injecting an amount smaller than the full compressor capacity, in case this may prove satisfactory, intermittent operation is recommended. Since the detention time through the 2,000-foot aerated section of the siphon is 22 minutes, satisfactory intermittent operation may be provided by a timer that will start the compressor every five minutes and an interval timer that will allow it to run for intervals that can be adjusted from 1 to 5 minutes. In operation, different running times will be tried until a satisfactory result is obtained. The air requirement may be varied seasonally. Alternatively, install two compressors to supply, respectively, 6 cfm and 10 cfm, then operate either or both as indicated by experience.

5.1.3 Injection of Oxygen into Force Mains

If a force main has very little rise, it may be difficult to dissolve enough oxygen by air injection to accomplish sulfide control. Use of commercial oxygen is a possible alternative to air since the rate of dissolution of oxygen is thereby increased. Oxygen may also be serviceable as an alternative to air in force mains of irregular profile, provided that all of the oxygen can be kept in solution, and it may be an important aid where maximum BOD reduction is desired. Due to cost, it is important that the injection of oxygen into force mains be done in a way that does not allow part of it to escape unused.

Information on the use of oxygen in a force main has been reported by the Water Pollution Research Laboratory at Stevenage, England (4). The rise of the main is 90 feet. Oxygen is supplied at a dosage of 75 mg/l and complete dissolution is accomplished by feeding it into the pump. In contrast to the practice where air is used, oxygen is supplied only while the wastewater is being pumped into the main. In this manner all of the wastewater is given a fixed dosage of oxygen. Residual dissolved oxygen at the end of the main averaged 16 mg/l. Of the oxygen used, 28 mg/l reacted in the stream and 30 mg/l reacted on the slime layer.

The Stevenage work illustrates the value of oxygen injection where maximum BOD reduction is desired, because the rate of reaction on the pipe wall is proportional to the oxygen concentration (5). Also a higher oxygen concentration can be carried as a reserve in the wastewater leaving the end of the force main. Wastewater containing the normal concentration of nitrogen can carry, in addition, 15 to 20 mg/l of oxygen without bubble formation or significant loss if the water does not cascade. The use of air in a force main can seldom produce a residual of more than 2 to 4 mg/l of oxygen.

Another method of accomplishing complete dissolution of oxygen is the use of a U-tube through which the water would pass before entering the force main. This is discussed in detail in Section 5.1.5.

5.1.4 Falls

Drops, or falls, and other places of high turbulence are notorious for release of odors from wastewater, including hydrogen sulfide if any is present, and for the consequent corrosion of susceptible structures. At the same time, falls cause dissolution of oxygen, which, given a little time, will destroy the sulfide remaining in the stream. The amount of oxygen absorbed by a series of falls is much larger than the amount absorbed by the smooth flow of the water through the same loss of elevation (6). Thus, points of turbulence can be both harmful and beneficial.

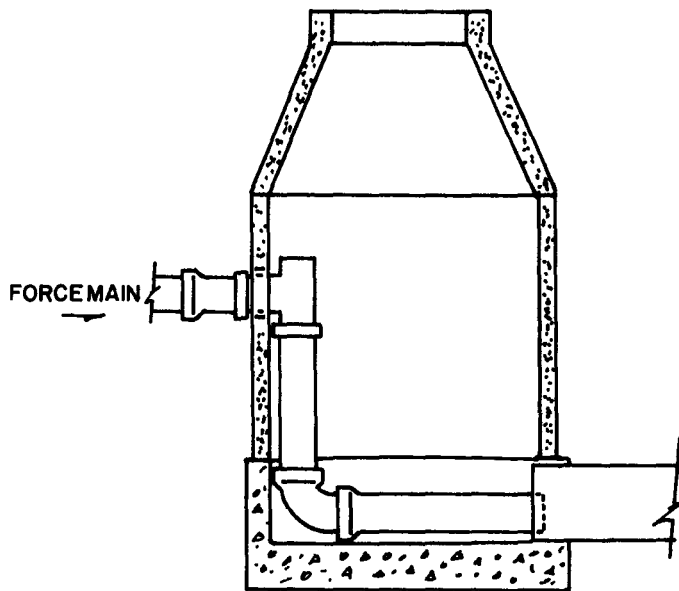
It is possible to preserve the benefits of a fall while guarding against harmful effects even where H_2S is present. This means that corrosive and odorous gases must be trapped in some way. Sometimes this can be done quite simply and inexpensively, as illustrated by the following discussions.

The Sacramento County Sanitation Districts (California) had a force main discharging into a manhole at an elevation four feet above the invert. The manhole is the temporary upper terminus of the sewer. Sulfide concentrations in the wastewater were not very high, generally less than 1.0 mg/l, but the turbulence of the fall released so much H_2S that there were odors in the vicinity and serious corrosion of the manhole. To remedy this condition, the Districts installed a PVC drop pipe essentially as shown in Figure 5-2. Air is drawn down the pipe by the falling water, and as the water leaves the pipe at high velocity it drives the air on down the sewer. There is no recycling of air into the manhole; rather, additional air is drawn into the sewer. The manhole is now dry and completely free of odor. The sewer is made of vitrified clay pipe, and is unharmed by the H_2S . By the time the wastewater reaches the next manhole the sulfide has been completely oxidized.

Two features of the installation should be noted: 1) the discharge of the drop pipe is inside the sewer that carries the wastewater away, and 2) the bottom of the drop pipe is a smooth curve, so that the wastewater conserves its momentum and discharges at high velocity.

Pressure mains are commonly designed so that they enter the receiving manhole close to the bottom. By minimizing the fall the problem of possible H_2S release is minimized. However, by properly trapping the released gases, and by confining them in a corrosion-resistant structure, as shown in Figure 5-2, the drop becomes a desirable feature.

FIGURE 5-2
 H_2S – CONTROLLING DROP STRUCTURE
AT THE END OF A FORCEMAIN



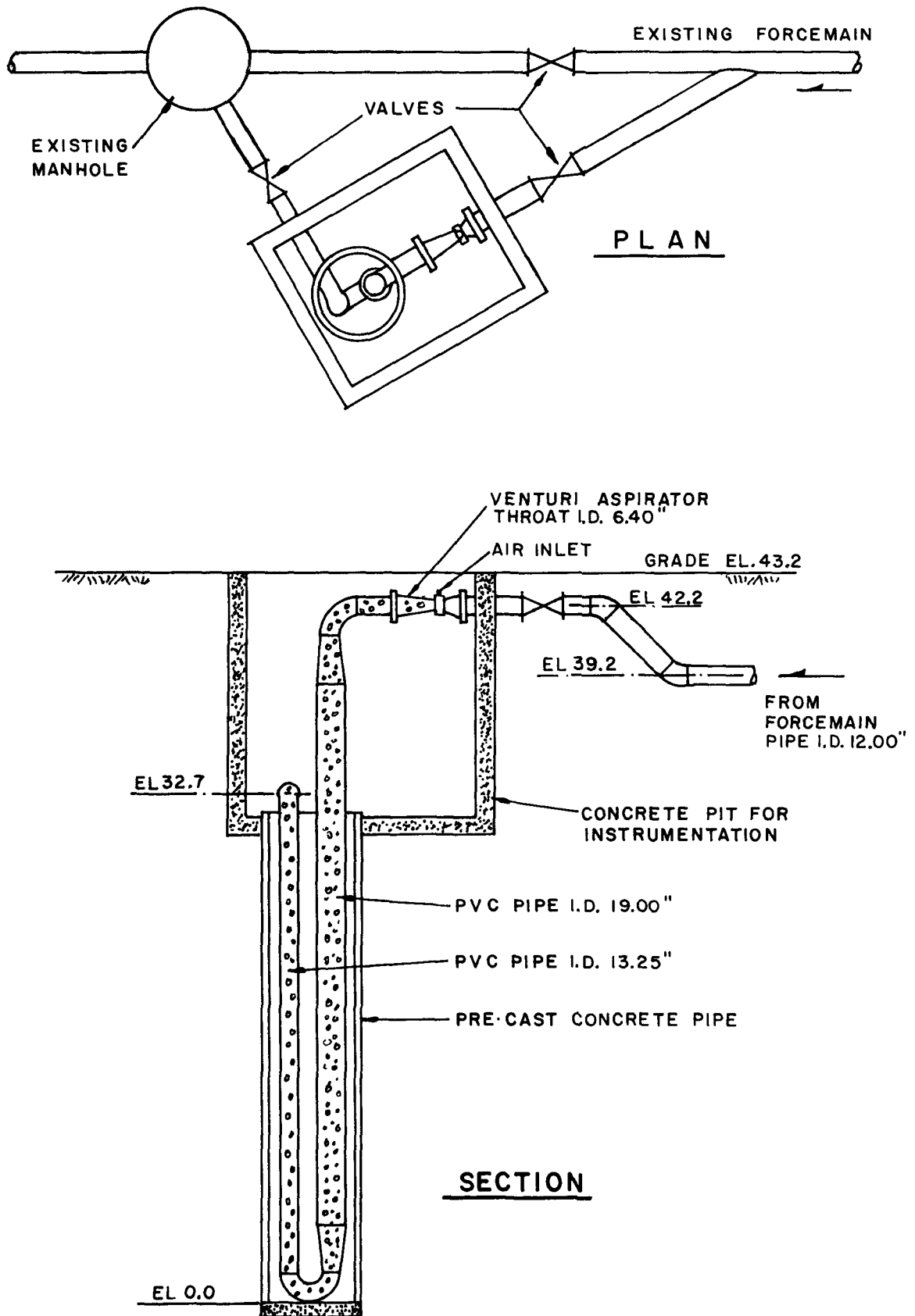
It may sometimes be advantageous, therefore, to purposely raise the end of a force main several feet higher than the bottom of the manhole, so as to use this simple and inexpensive method to dissolve oxygen and prevent sulfide problems.

5.1.5 U-Tube Aeration

5.1.5.1 Basic Concept

Basically, a U-tube consists of two vertical pipes connected by a U-bend at the bottom (literal U-tube) or other functionally equivalent arrangement, including concentric pipes. Air or sometimes oxygen, is dispersed into the wastewater in the descending leg, being carried through the U-tube with the water, as shown in Figure 5-3. The relatively long

FIGURE 5-3
U-TUBE DESIGN, JEFFERSON PARISH STATION 5



contact time of the gas with the water and the increased pressure at the bottom due to the water column make the U-tube an efficient aeration device. If sulfide is present in the wastewater entering the U-tube, the oxygen that is absorbed will oxidize it, to some extent in the U-tube but mostly in the downstream sewer. Where no sulfide is present, a U-tube may nevertheless be used to provide a dissolved oxygen reserve to sustain aerobic conditions downstream.

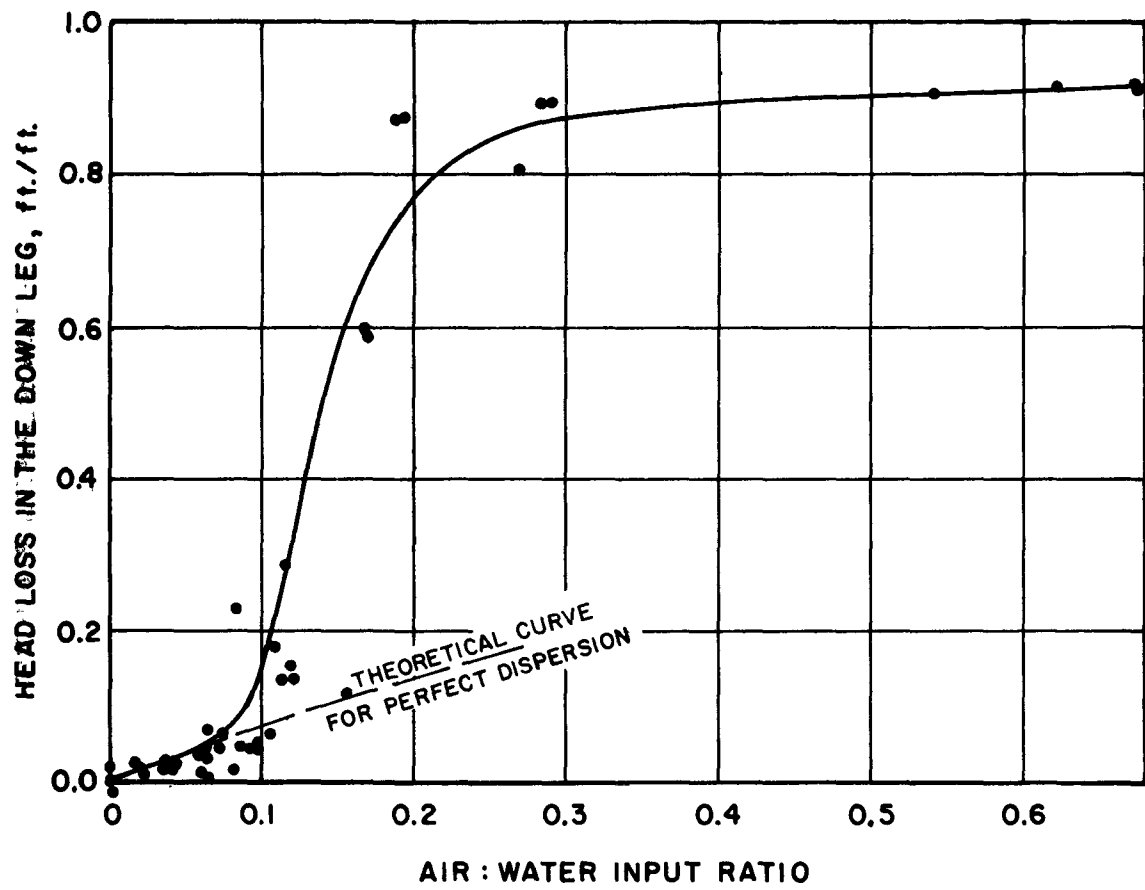
5.1.5.2 Variations

There are basically three ways that air can be supplied to a U-tube: 1. A venturi aspirator may be placed in a pipeline leading to the U-tube, as shown in Fig. 5-3. This is a suitable installation at the end of a pressure main. The venturi not only supplies air to the U-tube, but also provides an initial intimate mixing of the air with the wastewater. The throat must be small enough so that the negative pressure will aspirate the required amount of air at times of minimum flow, yet not cause excessive head loss during maximum flow. These conditions are difficult to meet where there is any substantial back pressure at the venturi discharge (7). The venturi is a practical device to aspirate air if it can be placed higher than the hydraulic head at the U-tube outlet. Sometimes this may mean raising the venturi out of the ground.

If air in moderate amount is suitably diffused and the velocity in the down leg is not too slow, the air remains dispersed. If the air input is increased, a condition is reached in which a pocket of air is formed in the top, which may soon largely fill the column. Evidence of this effect is seen in Figure 5-4 which shows the head loss in the down leg of the U-tube shown in Figure 5-3. For each experimental condition, the total head loss measured between two pressure taps in the down leg has been divided by the vertical distance to show the average energy loss in ft of wastewater per ft. Also, the theoretical head loss has been calculated on the assumption of perfect dispersion of the air and a 0.2 ft/sec rate of rise (slip velocity) of the air bubbles through the wastewater. The compression of the gas was taken into account, but no correction was made for the amount dissolving. This calculated loss is shown as a broken line. The experimental points are scattered because of the difficulty of getting steady pressure readings but it is clear that a major departure from the theoretical curve for complete dispersion of the air begins when the air input exceeds 10 percent of the wastewater flow. Soon the wastewater behaves almost as though it were in free fall, where the head loss approaches 1.0 ft/ft of fall. In these tests, the U-tube operated with a nominal downward water velocity of 1.5 ft/sec. If water velocity had been quite slow, it can be assumed that an air pocket would have formed at a lower air-water ratio. Also, if the air had been ineffectively dispersed, so that it was present as relatively large bubbles, there would have been a greater tendency to form an air pocket.

Another way to supply air or oxygen to a U-tube is by injecting it under pressure into the top of the descending leg. Even with a diffuser ring, a gas pocket is expected if the gas input is more than 10 percent of the wastewater flow. The wastewater will fall through this space, and gas will be entrained by splashing and will be carried through the U-tube.

FIGURE 5-4
HEAD LOSS IN DOWN LEG OF 42 FT U-TUBE



By injecting gas under pressure the head loss through a venturi is reduced, but this reduction may be more than offset by a greater head loss in the U-tube. The choice of a venturi or compressed gas will depend partly upon whether air or oxygen will be used, and also upon the required dissolved oxygen input and wastewater flow patterns. The compressed air or oxygen U-tube is likely to be most suitable for use at pump stations, especially in situations where the force main is nearly level and the discharge pressure is low. In this case ordinary air injection would be ineffective.

A third way to operate a U-tube is for entrainment alone to supply the air input, providing only an opening at the top to allow the air to enter. The amount of air entrained will be a function of the available head (net elevation loss). It is not likely that entrainment alone will meet the purposes of a U-tube if the head is less than 10 ft. No actual installations are operating in this mode.

In addition to the three ways discussed above for supplying air to a U-tube, there is also the possibility of forcing air into the rising leg. If no air is entrained on the inlet side, the device is a simple air lift pump or eductor which is discussed in Section 5.1.6. If there is air entrainment in a descending leg as well as air injection into the rising leg, the effect is a hybrid operation. This condition, too, will be considered under the heading of air lifts.

5.1.5.3 Design Considerations

The amount of dissolved oxygen that must be supplied to the wastewater, the available head, the quantity of flow, and variations of flow are factors that influence the design of a U-tube. The oxygen reaction rate of the wastewater (or the 15-minute "immediate dissolved oxygen demand") should be determined several times by use of an amperometric probe to ascertain average conditions and extremes. Similarly, sulfide conditions should be thoroughly explored.

For large flows, such as 25 cfs, concentric tubes could be used for the U-tube. For small flows, concentric tubes would probably lead to fouling with stringy material in the wastewater, so literal U-tubes are used. The rising leg must be small enough so that the velocity will carry away sand or small pebbles that may be in the wastewater. No difficulty has been experienced where the upward velocity is 4 ft/sec or more. Where the flow is variable, there will probably be no difficulty if the velocity reaches 4 ft/sec at least once each day. In the descending leg, a lower velocity is desirable to increase the time of contact of the air with the water.

In U-tubes presently in operation, the nominal average velocity in the descending legs, that is, average flow of wastewater divided by cross-section area of the pipe, is about 1.5 ft/sec. The depths of U-tubes now in use range from 17 to 54 ft.

The amount of oxygen dissolved per unit of energy dissipated increases with the height of the U-tube. However, nitrogen dissolves in increasing amounts too. As the water moves up the rising leg, the decreasing pressure allows these gases to come out of solution again.

The same effect in aerated pressure mains is discussed in Section 5.1.2. There is a U-tube depth beyond which there will be little further improvement in over-all efficiency. The economical optimum when using air is probably at a depth of 50 ft or more. With pure oxygen, the depth should be great enough so that the gas dissolves completely. A way to calculate the required height in this case is yet to be developed. If the applied oxygen is completely dissolved to produce a concentration of 15 to 20 mg/l (about 1 percent of oxygen by volume), with no supersaturation with nitrogen, practically no oxygen will be lost in the rising leg.

A basic requirement for U-tube aeration, as well as any other aeration device, is enough energy to mix the air with the water. The U-tube is equivalent to other aeration methods in this respect, and under favorable condition it is probably superior. Its usefulness does not rest upon any uniqueness in this respect, but upon simplicity and applicability where other methods might be unsuitable. However, the U-tube or some equivalent of a U-tube will have a major advantage where commercially pure oxygen is used in a wastewater collection system, because it is one way to provide the pressure that needs to be used in some manner to accomplish 100 percent utilization of the oxygen. Where oxygen is to be used, it is better to use a U-tube or other functionally equivalent pressure device rather than the systems usually adopted where the gas to be used is air.

A computer program has been developed for calculating the behavior of U-tubes supplied with air (7). A rough but conservative estimate of the amount of oxygen that can be dissolved in a U-tube under suitable operating conditions using air can be made on the basis of the net elevation loss or, conversely, an estimate can be made of the required elevation loss for any specified dissolved oxygen objective, using Table 3-1 as a guide.

If a U-tube is installed at the end of a pressure main, and if there was originally little or no fall at the end of the main, an increase of pumping head will be necessary to make the device work. Either back pressure will be produced by injected air, or the inlet to the U-tube will need to be raised to an elevation several feet above the outlet, or even raised out of the ground. If the pumps do not have the capability of pumping the wastewater against this head, it may be necessary to change impellers, and perhaps to change motors. Most commonly, pumping installations can accommodate the relatively small increase of head.

The following two case histories illustrate design and performance features of U-tubes using aspirated air, compressed air, and oxygen.

CASE HISTORY 1

Jefferson Parish, located on the west side of the City of New Orleans, is in an area of level terrain and high groundwater. The original sewer system was built with minimum slopes and with many pump stations. Sulfide odors and corrosion resulted. The most severe conditions were at force main discharges where the wastewater fell several feet into the manholes, and at pump stations where there was also splashing and release of odorous air:

Figure 5-5 shows the trunk sewers and force mains in the collection system where the installations were made. Average dry-weather flows, pumping rates in the force mains, locations of aeration devices, and sampling stations are indicated.

U-tubes were installed in 1970 at the ends of two force mains (Stations 5 and 7), and an air lift aerator was placed in a gravity sewer (Station 2). The project was undertaken by Jefferson Parish with the assistance of a research grant from the U.S. EPA (7).

Figure 5-3 shows the design of the U-tube at the end of the force main at Station 5. The U-tube at Station 7 follows the same general design, but the depth of the tube is 54 feet instead of 42, the U-tube legs are 12 and 8 inches in diameter instead of 19 and 13.25 inches, and the elevation difference from inlet of the U-tube to the outlet is 7 feet instead of 9.5 feet.

A significant improvement resulted at the ends of the force mains, since the water no longer fell several feet into the manholes. Sulfide and dissolved oxygen tests were made before and after activating the aeration devices. Results are shown in Table 5-2.

TABLE 5-2

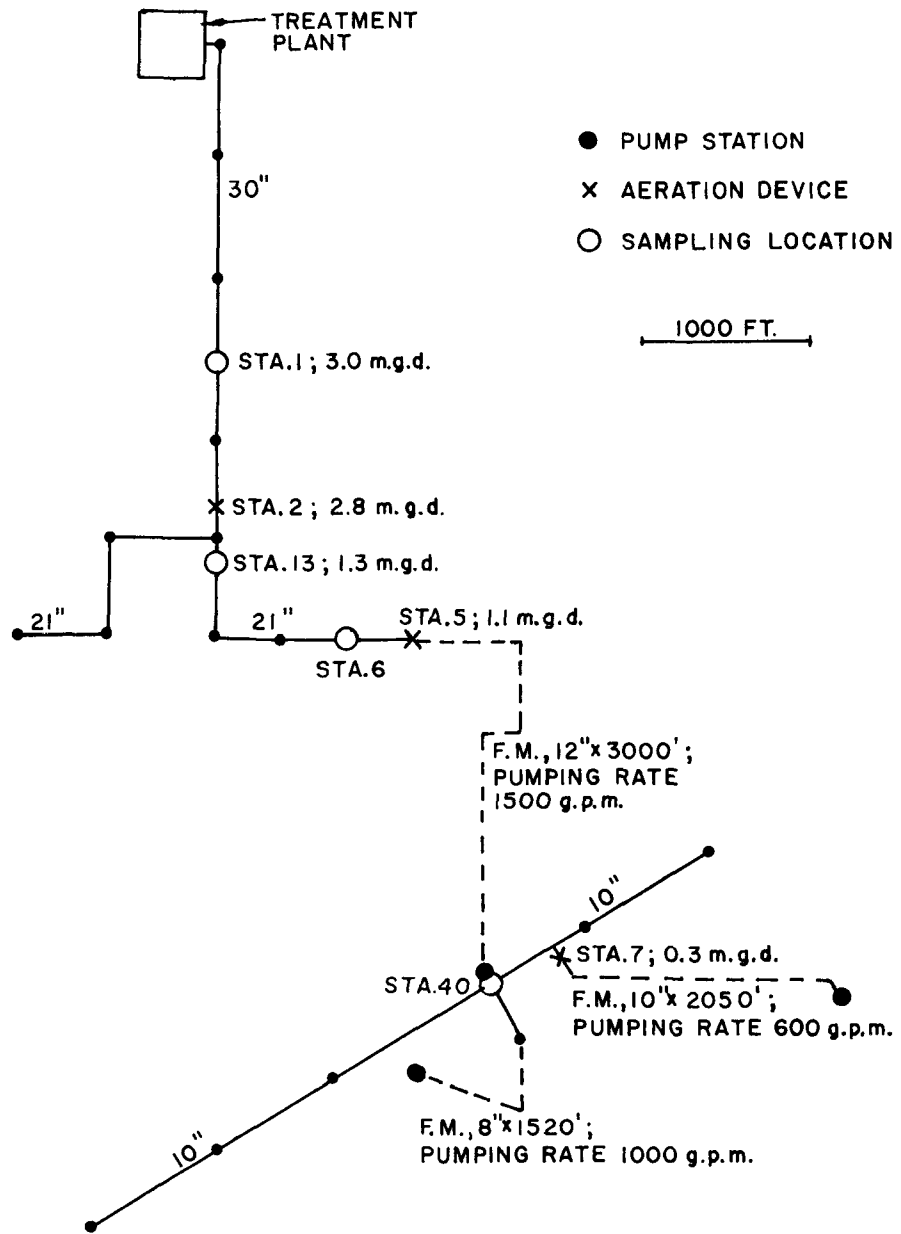
RESULTS OF U-TUBE OPERATION IN JEFFERSON PARISH, LA. (7)

Station	Before U-tube Use			During U-tube Use		
	No. Tests	Dissolved Oxygen mg/l	Dissolved Sulfide mg/l	No. Tests	Dissolved Oxygen mg/l	Dissolved Sulfide mg/l
7	6	0.6	0.26	22	2.1	0.06
40	34	1.9	0.42	10	2.3	0.11
6	32	0.8	0.51	9	1.6	0.05
13	24	0.0	0.30	27	0.7	0.02

The flow that passed through the U-tube at Station 5 constituted 89 percent of the flow sampled at Station 6, and 79 percent of the flow sampled at Station 13. Station 40 is a pump station wet well. From 40 to 85 percent of the wastewater sampled at that point had been aerated at Station 7, the proportion varying with the operation of the pump stations. This wastewater also received some aeration at the wet well, both before and during U-tube operation, by virtue of a fall of 3 to 6 ft.

At stations 7, 40 and 6, some dissolved oxygen was present without operation of the U-tubes but it declined to zero by the time the wastewater reached Station 13. With the U-tubes in operation, there was enough oxygen to prevent sulfide buildup and sulfide was reduced to zero at Station 13 except for a few hundredths of a milligram per liter on a few occasions, and one reading of 0.23 mg/l.

FIGURE 5-5
MAIN TRUNKS RELATING TO U-TUBE INSTALLATION
IN JEFFERSON PARISH



Station 2 was an air lift alongside the sewer, mentioned in Sec. 5.1.6. It was operated for only a short time; performance data are not available.

The 1970 installations costs for the U-tubes were:

Station 5—Aspirated-air U-tube installed on end of 12-in force

main, depth = 42 ft, \$16,000

Station 7—Aspirated-air U-tube installed on end of 8-in force

main, depth = 54 ft, \$11,000

CASE HISTORY II

The City of Port Arthur, Texas, is located on terrain similar to that of Jefferson Parish, Louisiana. According to prevailing standards in the area, most of the sewers were laid to flow at velocities of 1.6 ft/sec when half full. The system includes 12 principal pump stations, and as many more smaller ones. The discharge piping is very short in many cases, the stations serving only as lifts. One force main 5,427 ft in length has produced sulfide at an average concentration of 15 mg/l, causing very severe problems, and three others of lesser lengths are important contributors. Nineteen sets of sulfide tests at various other places in the system showed concentrations averaging 3.1 mg/l. Records of 10 corrosion failures of concrete sewers indicated corrosion rates averaging from 0.08 to 0.17 in/yr. An eleventh sewer, 30 in. in diameter, failed in five years, with an indicated corrosion rate of 0.55 in/yr.

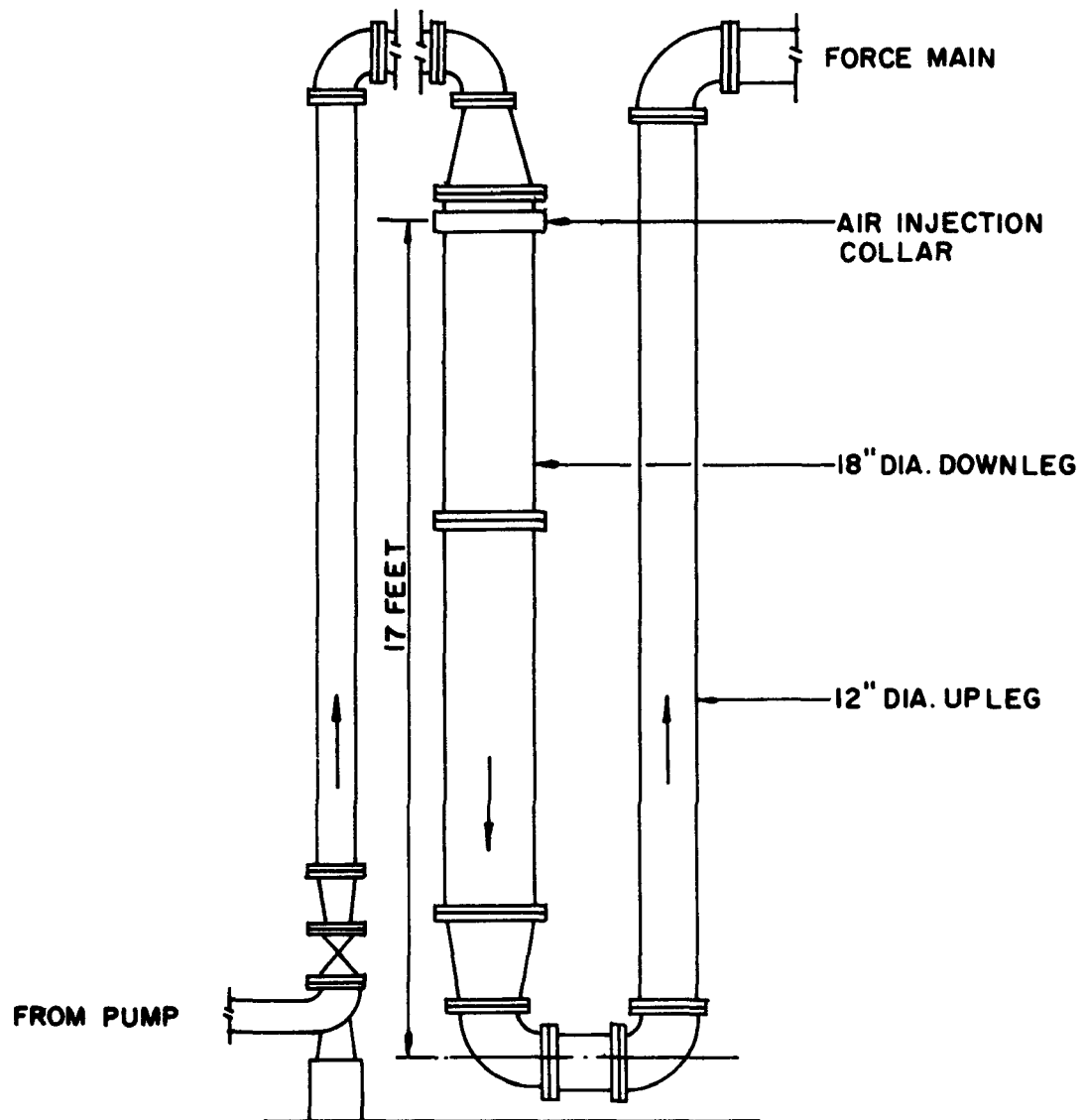
In a project made possible by a research grant from the U.S. EPA, several different schemes were tried out for supplying oxygen to the wastewater (8).

Two U-tubes were installed in 1967 at Pioneer Park lift station and two at Lake Charles lift station. In both of these locations the discharge piping is short; therefore the problem is not one of sulfide buildup in pressure mains. The objective of the U-tubes in these locations is to supply enough oxygen to oxidize the sulfide already present and to provide an excess to maintain aerobic conditions for some distance downstream.

In both cases the U-tubes are installed in the dry wells, which impose height limitations. Figure 5-6 is a representation of one of the U-tubes at Pioneer Park Lift station.

Venturi aspirators are not used in these installations. At Pioneer Park compressed air is fed to collars around the down legs of the U-tubes, whence it is diffused into the water by way of thirty-two $\frac{1}{8}$ -in holes. At Lake Charles lift station oxygen is diffused into the U-tubes by way of perforated copper tubes inserted into the pipeline at an angle directed downstream.

FIGURE 5-6
U-TUBE CONFIGURATION, PIONEER
PARK LIFT STATION



At Pioneer Park lift station, injection of an amount of air equal to 8 percent of the wastewater flow resulted in the dissolving of about 4 mg/l of oxygen. The head loss through the system was about 6 ft greater than when no air was used. During eight test at different air rates the sulfide concentration at the pump discharge averaged 3.4 mg/l, and at the discharge of the U-tube it averaged 2.0 mg/l. The difference is probably a reflection of the reaction rate between sulfide and oxygen. The reaction of sulfide with dissolved oxygen no doubt continues in the sewer. Odor conditions at downstream stations are, in fact, much better than formerly.

At Lake Charles lift station, where commercial oxygen is used instead of air, the dissolution of oxygen at various injection rates was as shown in Table 5-3.

TABLE 5-3
OXYGEN DISSOLVING EFFICIENCY

<u>Oxygen applied</u> mg/l	<u>Oxygen dissolved</u> mg/l	<u>Oxygen dissolved</u> percent
6.3	4.1	65
12.5	6.0	48
18.8	7.6	40
25.1	9.6	38

Sulfide concentrations in and out of the U-tube averaged 3.2 mg/l and 2.2 mg/l respectively. Variations of oxygen injection rate had no significant effect on sulfide concentrations at the U-tube discharge. However, at the highest oxygen injection rate the amount of oxygen remaining at the U-tube discharge was apparently 5.5 mg/l, which probably destroys the sulfide entirely in the downstream sewer.

5.1.6 Air Lifts

A U-tube in which the outlet is at an elevation equaling or exceeding the elevation of the inlet, with air injected into the rising leg, is an air lift. Air lifts deserve more consideration than they have received for use in low-lift pump stations. Their power efficiency as pumps is low, but part of the lost energy is the result of slippage of air bubbles past the water. This slippage greatly increases small-scale turbulence, resulting in the dissolving of oxygen from the air. If the combined effects of pumping and aeration are considered, the efficiency looks much better.

A zero-head air lift (inlet and outlet at essentially the same elevation) can be installed as an aeration device alongside an existing sewer. In this case the water level would be drawn down in the descending leg, so that wastewater would cascade into it. A partial dam would prevent recycling of the water, or perhaps permit a limited amount of recycling.

An air lift was installed along a sewer in Jefferson Parish, Louisiana. It was designed to raise the wastewater above the elevation of the top of the sewer and let it fall back into the sewer. The operation was objectionable because of odors produced by the air exhaling from the sewer. This condition can be avoided if the compressor takes suction from the atmosphere of the sewer. H_2S in the air supply rarely has any effect on the compressor, because the temperature of the compressor is high enough to prevent any condensation. Droplets of wastewater must be kept out by proper filters.

As far as is known, no zero-head air lift aerator has been installed. The amount of oxygen that would be dissolved can probably be estimated by calculating the potential power of the compressed air (see Sec. 5.1.2.2), converting that power to a height of fall of the wastewater stream, and using Table 3-1 to obtain an estimate of the expected percent of the oxygen deficit that will be satisfied.

5.1.7 Aeration in Wet Wells, Special Tanks, and Retention Basins

5.1.7.1 Basic Concept

Since sulfide in wastewater can be oxidized by the introduction of oxygen, aeration in tanks affords another way to destroy sulfide originating from an upstream source. The addition of even a small surplus of oxygen by this method may preserve an aerobic condition downstream where sulfide might otherwise appear. The tank used for aeration may be a pump station wet well.

5.1.7.2 Basis of Design

Wet wells of pump stations frequently have been the cause of odor nuisances. The splashing of the wastewater as it enters the well releases odors, especially if sulfide is present, and the escape of air brought into the wet well by the sewer and the air displaced as the wet well is filling disperse the odors into the atmosphere. Such odors have given rise to the belief that the wet well is the site of sulfide generation, but rarely is this the case. More commonly, sulfide concentrations decline because of the aeration of the entering water. Sulfide buildup in the unaerated wet well is not likely to occur unless the detention time is at least two hours, and the amounts produced are small unless the detention time is many hours. Use of pump station wet wells as aeration basins is becoming more common, but no data on operating installations are available. The basic theory for such an operation is now better understood, so that installations can be rationally designed.

If water containing sulfide flows into a basin where it has a detention time of only a few minutes, and it is aerated there, objectionable amounts of sulfide will be released into the atmosphere. If the detention time is longer, say a half hour, oxidation can generally be carried to the point where sulfide concentrations will be close to zero. Sulfide in the incoming stream will be diluted to a low level and held there by a rate of oxidation equaling the rate of addition.

If aeration is to be undertaken in an existing wet well, the detention time should be maximized by setting the controls on the pumps so that the well is not pumped down very far. Tests should be made on the influent wastewater to determine temperature, sulfide concentrations, rate of oxygen consumption, and rate of oxidation of sulfide. These characteristics will vary diurnally, so should be determined at different times of the day. They also vary seasonally. It is most important to know or to estimate the characteristics of the wastewater at the season of maximum temperature. With this information, the oxygen requirement can be determined and used as a basis for design of the aeration facility.

If the average detention time in the wet well is not long enough to effect substantially complete sulfide oxidation, aeration may nevertheless add enough oxygen so that the reaction will be complete in the discharge main or in the downstream sewer. In this case, protective measures will be needed against corrosion and odors due to H_2S in the wet well.

If the wastewater is free of sulfide, detention time is not important except insofar as it is involved in getting the desired amount of oxygen into solution.

If aeration in a wet well is undertaken, it will usually be by use of spargers or diffusers. The installation would be designed so that the compressor takes suction from the atmosphere of the wet well to minimize the escape of odorous air. Impurities in the air will not harm the compressor if particulate matter is filtered out. The possibility of excessive depletion of oxygen in the reused air may need to be considered, but this will rarely be a problem, especially if the water level fluctuates due to intermittent pump operation.

Another way to accomplish aeration in the wet well is to maximize the fall of the incoming water. This may be accomplished by proper adjustment of the pump controls to keep the water level as low as is practical. This will require more frequent starting and stopping of the pump, but this does no harm and does not materially reduce the efficiency if the pumping intervals are not too short. A running time of 2 to 3 minutes at each pumping is suggested as a reasonable minimum.

The method of maximizing the fall of the water is suitable where the incoming water contains no sulfide, or very little, and the objective is to augment the oxygen supply. Table 3-1 shows the oxygen uptake that may be expected. The amount may not seem large, but it can effect a substantial improvement in downstream sulfide conditions.

An alternative to the use of a wet well as an aeration basin is the construction of a special tank. A steel tank erected for this purpose adjacent to a pump station at Port Arthur, Texas, is shown in Figure 5-7. Aeration of the high-sulfide sewage in the wet well was considered undesirable because of odor release in this location. Wastewater is pumped from the wet well into the tank, where it is aerated. Part of it then falls back into the well. The wastewater is kept aerobic and the detention time is long enough so that it is essentially free of sulfide. Sulfide conditions are greatly improved downstream.

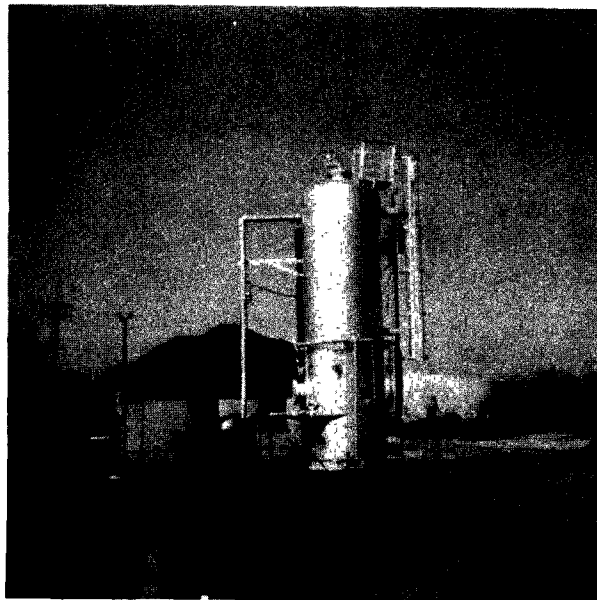
Basins are sometimes constructed in large sewerage systems to equalize diurnal flow variations. Adequate aeration is normally applied to control sulfide generation and to provide mixing energy to minimize the settling of solids. Overflow basins to retain storm flows are sometimes aerated for the same reasons.

5.1.8 In-Line Augmentation of the Oxygen Supply in Gravity Sewers

5.1.8.1 Basic Concept

The difference between a condition of sulfide buildup and one of no buildup is often attributable to a quite small difference in the oxygen supply. Consider a sewer 3 feet in diameter at a slope of 0.0012 flowing half full at a velocity of 3.4 ft/sec. If the dissolved oxygen concentration is near zero, the rate of supply by surface aeration is 1.6 mg/l-hr. For $EBOD = 350$, the expected rate of sulfide buildup if no sulfide is present initially will be 0.52 mg/l-hr. The rate of oxygen supply that would hold sulfide concentrations to a few tenths of a milligram per liter would be roughly 2.0 to 4.0 mg/l-hr, or 1 to 2 mg/l per mile of flow. Thus, aeration devices capable of supplying oxygen supplements of 1.0 mg/l at 1-mile intervals would probably prevent sulfide buildup. The importance of such small oxygen increments is demonstrated by the evident role of junctions and other points of turbulence in curbing sulfide generation.

FIGURE 5-7
AERATION TANK AT PUMP STATION,
PORT ARTHUR, TEXAS



If in-line oxygen supplementation is to be undertaken, a decision as to the amount of oxygen to apply must be made, and this requires that the objectives be clearly stated. The purpose might be only to destroy the sulfide already present in the stream, or it might be desirable to provide a surplus of oxygen to sustain aerobic conditions for a certain distance downstream. Another possibility that may be considered is the maximizing of BOD reduction. This would be beyond the requirements for sulfide control, but if oxygen is to be supplied, the chance to attain a significant reduction of BOD at the same time should not be overlooked. In large trunk sewers, the wastewater may develop a capability to use oxygen at a rather high rate, as previously shown by Figure 3-9. In smaller trunks, oxidation on the slime layer may be a major factor, especially if the oxygen concentration is kept high (4) (5). Thus, an important degree of BOD reduction is possible if an aerobic condition is sustained by repeated oxygen feeding.

Before making design decisions for a facility to supply dissolved oxygen, it would be desirable to test the wastewater several times at various times of the day and preferably at different seasons, to determine sulfide concentrations, oxygen reaction rate in the wastewater, and rates of oxidation of sulfide. Then the desired rates of oxygen input can be determined, and the oxygen-supplying facility can be designed accordingly.

If the objective is only to destroy a certain amount of sulfide already present in the wastewater, it generally will not require more than four pounds of dissolved oxygen for one pound of sulfide, and sometimes only two for one. The maintaining of enough oxygen in the water to prevent sulfide buildup in a typical case is likely to require an oxygen supply only a half or a third as great as the oxygen reaction rate of the wastewater in the presence of an excess of oxygen.

5.1.8.2 Possible In-Sewer Methods for Adding More Oxygen to the Stream

Various methods for in-sewer aeration have been considered, including diffused air by way of a perforated pipe along the bottom of the sewer, aeration in the bottoms of manholes, and mechanical aerators. As far as is known, no process of this type is in operation, and the prospects for practical application do not look promising.

The use of commercial oxygen has also been explored. It has a number of advantages in comparison with air for in-sewer application.

One idea for applying pure oxygen is to use it to enrich the sewer atmosphere. The effect of a pure oxygen atmosphere over a short distance, however, would be negligible. In the very large trunks a pure oxygen atmosphere would not prevent oxygen starvation in the stream. The practical problems of attempting to fill the free space in a major trunk sewer with oxygen and maintaining it there without excessive losses appear insurmountable, and even if it could be done, the expected benefits would not be commensurate with the cost.

The bubbling of oxygen into the wastewater stream would be inefficient, since most of the oxygen would escape unused. The enriched sewer atmosphere could be recompressed and diffused into the water again, but it does not seem likely that this would be a practical operation.

A method that does show promise for adding pure oxygen to the stream in a free-flowing sewer is to produce a high concentration of oxygen in a side stream under pressure, and then release this to the main flow. An essential feature of the method is the maintenance of full pressure all the way to a submerged nozzle where the oxygenated water escapes at high velocity. In this way no oxygen can come out of solution in the piping, and the high velocity of the jet causes immediate dilution with a large volume of the main flow, so that no bubbles are formed, or only extremely small bubbles that immediately redissolve.

The method was first employed in 1970 to supply supplemental oxygen in a small privately owned wastewater treatment plant in the City of Simi Valley, California. Preliminary experiments with the method have been conducted recently in a sewer of the Los Angeles County Sanitation Districts.

Figure 5-8A is a schematic drawing of a design corresponding in its main features to the tank shown in Figure 5-7, but modified to be suitable for the production of a concentrated oxygen solution. Figure 5-8B shows the design of the tank used for this purpose at Simi Valley. In this design the pumping rate into the oxygen-dissolving tank is constant, but the oxygen supply can be varied. At a low oxygen input rate, the water level is high in the tank. If more oxygen is supplied, the water level is depressed until the increased turbulence due to the fall of the water suffices to dissolve the oxygen as fast as it is supplied. There is, of course, an upper limit to the amount that can be dissolved, depending upon the pressure and the flow of water, and to some extent on the height of the tank.

Figure 5-8C shows how one of these oxygen-dissolving units could be used for applying oxygen to the stream in a trunk sewer.

The nozzles through which the oxygen solution is released into the main wastewater stream must be of a size matched to the characteristics of the pump for maximum efficiency. A small flow of water at a pressure as high as several hundred psi might be used, or a large flow at relatively low pressure. If a high-pressure oxygen solution is prepared, use might be made of treatment plant effluent or water from any other available source, pumped to points of application before or after charging it with oxygen. If raw wastewater is used for surcharging with oxygen, the nozzles would have to be large enough so that they would not clog with solids, which would favor a low-pressure, high-volume system. In the experimental installation of the Los Angeles County Sanitation Districts above referred to, screened wastewater from the sewer was used.

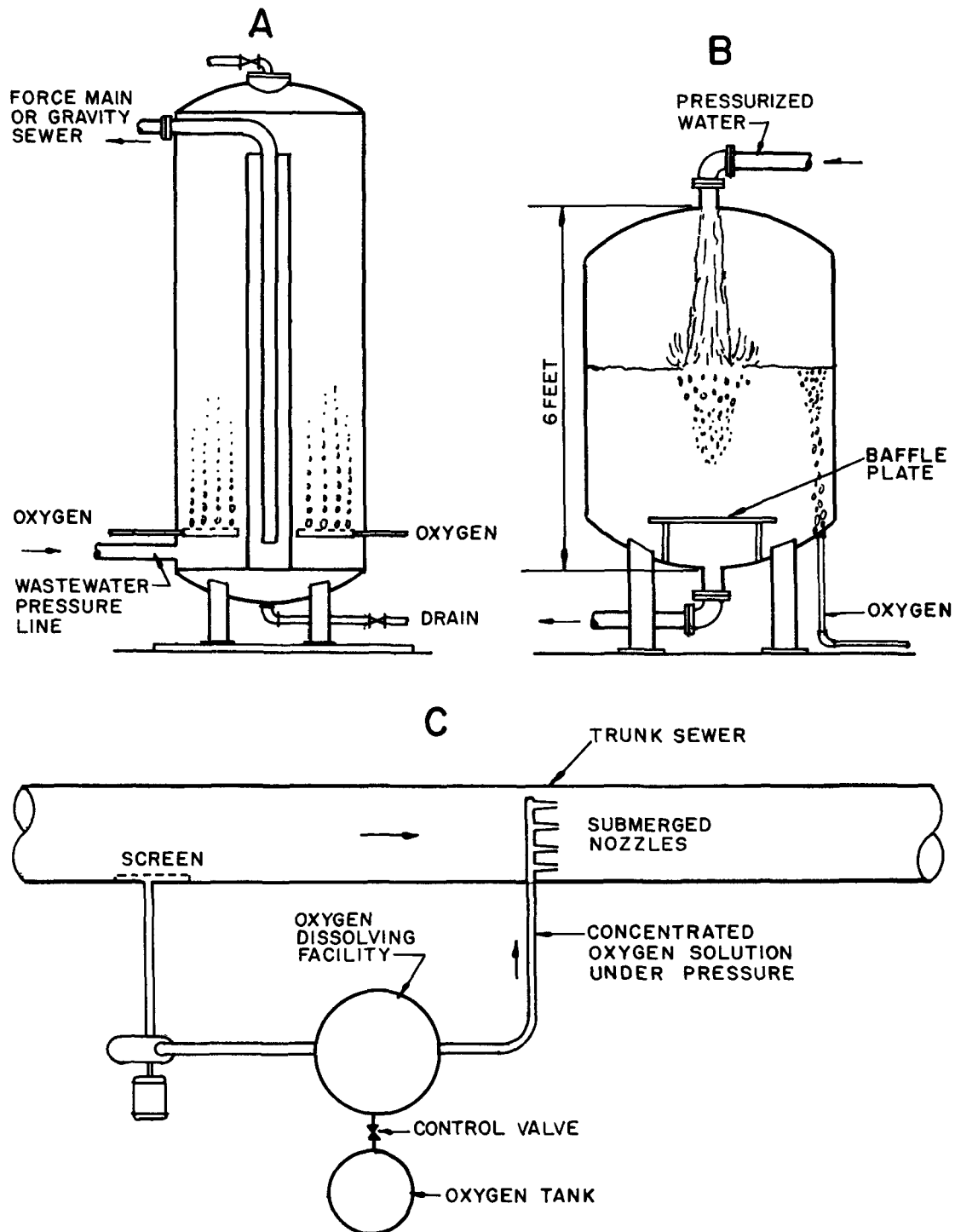
The pumping action of the jets in a large trunk sewer could add enough kinetic energy to the main stream to significantly increase the capacity of the trunk.

5.1.9 Ventilation

Ventilation of sewers is sometimes practiced. There are six possible objectives:

1. to increase the oxygen content of the sewer atmosphere;

FIGURE 5-8
TWO TYPES OF PRESSURE TANKS FOR DISSOLVING
OXYGEN AND IN-SEWER APPLICATION OF OXYGEN



2. to remove as much H_2S as possible from the sewer before it is oxidized to H_2SO_4 ;
3. to dry exposed surfaces of the sewer structures, thereby preventing oxidation of H_2S to H_2SO_4 ;
4. to eliminate toxic atmospheres in the sewer;
5. to remove explosive atmospheres in the sewer;
6. to control odors otherwise escaping from the sewer in sensitive areas.

Only the first of these six objectives is related to improvement of the oxygen balance, but because of the interrelationships, all aspects of ventilation will be discussed in this section.

5.1.9.1 Ventilation to Combat Oxygen Depletion in Sewer Atmosphere

The usefulness of efforts to prevent oxygen depletion in the sewer atmosphere in any particular case must be viewed with due regard to the significance of the problem to be solved. In reality, the depletion of oxygen in the sewer atmosphere is insignificant under most circumstances. In some cases, such as a blockage of the air stream by a surcharged section of sewer, as much as half of the oxygen in the sewer air must be used up, and the concentration of course could approach zero in a completely isolated air space. In partly filled sewers, however, air is displaced by the rise and fall of the fluid level, and there is normally a downstream flow of air in the sewer. In such sewers, oxygen concentrations are rarely less than 90 percent of normal, and for the most part they are in the range of 95 to 100 percent.

Before a decision is made to ventilate a sewer, tests should be made to determine the prevailing oxygen concentrations. *If the concentration is above 90 percent of normal, that is, 19 percent O_2 in the sewer air, ventilation will not make any material difference in the oxygen balance in the wastewater stream.*

5.1.9.2 Ventilation to Reduce H_2S Concentrations

The effects of ventilation on rates of production of acid on sewer wall, and hence on rate of corrosion of susceptible materials, are more complex. There is no doubt that ventilation can reduce H_2S concentrations in the sewer air. The reduction, however, is due in large part to the increased turbulence of the air, and the consequent increase of the coefficient of mass transfer of H_2S from the sewer atmosphere to the exposed pipe wall. Near the point of ingress of fresh air, the H_2S content of the sewer air may be greatly diluted and the rate of corrosion reduced, but remote from the fresh air source the H_2S content of the air approaches the steady state concentration fixed by the equality of the rate of escape from the water and the rate of oxidation on the wall. The rate of acid production on the pipe wall is then controlled by the rate of escape of H_2S from the stream, not by the concentration of H_2S in the air.

In determining the possible effect of ventilation, it is useful to estimate the rate at which a steady state of H_2S concentration is approached in a sewer atmosphere. Consider a reach of 48-in sewer in which the atmosphere is suddenly replaced by fresh air. It is estimated that in a 48-in sewer flowing half full the concentration of H_2S would increase to one-half of the steady state condition in 20 minutes after the air change. If a ventilation system is moving the air through the sewer at a velocity of 1 ft/sec, this condition would be reached in 1200 ft. If the air were completely removed from the trunk every 1200 ft and replaced with clean air, but with no change of air velocity, the rate of corrosion at the downstream end of each reach would be half as fast as it would be without the exchange of air. If the rate of ventilation were increased, the distance to approach half way to the steady state would be increased, but not proportionally. In smaller trunks the distance required to approach half way to the steady state H_2S concentration in the air would be shorter and in larger trunks it would be longer.

The estimate is very rough, but with any other reasonable assumptions it would still appear that *complete replacement of the sewer atmosphere with fresh air at rather frequent intervals would be necessary if removal of H_2S by ventilation were relied upon for a major reduction in corrosion rates.*

5.1.9.3 Ventilation to Dry the Sewer Wall

Hydrogen sulfide does not cause corrosion of concrete if the surface is dry, because the bacterial oxidation of H_2S can occur only in the presence of moisture. Therefore ventilation has sometimes been undertaken with the objective of drying the walls. Thistlethwayte (9) estimated that the relative humidity of the air should not be higher than 85 percent if protection is to be assured. A structure close to a point where ventilation air enters a sewer can be dried satisfactorily, but it is not possible to continuously dry any great length of sewer even in dry climates. *Not even the usual distances between manholes can receive year-around protection by attempted drying of the walls.*

5.1.9.4 Ventilation to Prevent Lethal Atmospheres

The atmospheres in sewers are sometimes lethal, usually because of the presence of hydrogen sulfide. Rarely, oxygen impoverishment of the air or the presence of other toxic gas may be the causes of deadly atmospheres. Adequate ventilation of a manhole or junction chamber by means of a blower will provide air safe to breathe, but it would be difficult to assure safety between manholes by this means. *In no case would it be feasible to keep a whole sewerage system continuously ventilated in the hope that workmen could enter without safety precautions.*

5.1.9.5 Ventilation to Prevent Explosive Atmosphere in Sewers

Much the same considerations apply to ventilation to remove explosive atmospheres. Explosions in sewers have resulted from leaking gas mains and from volatile hydrocarbons discharged into sewers, but not from gases produced by the sewage, unless possibly from

large accumulations of actively digesting sludge overlain by a stagnant atmosphere, a combination of conditions that can be imagined in a sewer only under very unusual circumstances. Occurrences of explosive atmospheres are infrequent and largely unpredictable. *Protection against explosions cannot be assured by any practical ventilation program.*

5.1.9.6 Ventilation as an Odor Control Measure

In some situations, the withdrawing of air from a sewer is a useful way to eliminate nuisance conditions that would arise from the uncontrolled escape of odors at other places (10). The air so withdrawn must be properly disposed of. The principal place that this is practiced is at wastewater treatment plants where air is withdrawn from the end of the sewer rather than to let it escape to the atmosphere. *Odor control is the only objective likely to be effectively served by continuous ventilation.*

5.1.9.7 Objections to Ventilation

Generally ventilation is undesirable because it increases the discharge of odorous air to the environment. Elaborate measures have been taken to deodorize air vented from sewers, but these processes have often been quite expensive and not entirely effective. Where air is withdrawn for the limited valid purpose of odor control, the most effective method for deodorizing the air has proved to be biological oxidation, using activated sludge tanks, trickling filters, or soil beds (10).

5.1.9.8 Case Histories

In the City of Los Angeles the North Outfall passes under Centinela Valley by way of a siphon 1,860 ft long. The exhalation of air upstream from the siphon caused serious odor problems. Closing tightly the inlet structure of the siphon only caused the air to escape from other structures farther upstream.

In 1958 the North Outfall was paralleled by the North Central Outfall, which also has a siphon, 8½ ft in diameter, under Centinela Valley. Paralleling this, however, an air by-pass 4 ft in diameter was constructed, carrying air from both of the major trunks into the North Central Outfall downstream from the siphon. Connections from the end of the trunk at Hyperion were then made to the suction side of the blowers for the activated sludge part of the treatment plant. Odors upstream from the siphons are completely eliminated, and odors at the plant are reduced to a negligible level. It had been shown in pre-design experiments that aeration tanks reduce the odor of the air to the same level as when pure air is used for aeration (10).

In the City of Palm Springs, California, a blower takes air from the end of the sewer and blows it through the rock in the trickling filter. This method is equally effective, and is now used in several places.

5.2 Chemical Methods

5.2.1 Basic Concepts

Chemicals can serve to control sulfide in either of two ways:

1. By reacting with any sulfide already present in the stream to prevent the escape of H_2S into the air. A chemical applied for this purpose may function in one of three ways. It may: a) oxidize the sulfide to sulfate or other intermediate oxidation products; b) convert dissolved sulfide to an inert metallic sulfide; or c) convert H_2S to HS^- .
2. By killing the sulfide-producing bacteria or by so altering the environment to which the slime layer on the pipe wall is exposed that it will not produce sulfide. The ways to do this include the adding of an oxidizing agent that raises the oxidation-reduction potential to a level where sulfate reduction is inhibited, or by adding a toxic substance that either destroys the slime layer or temporarily suppresses the activity of the sulfide-producing bacteria.

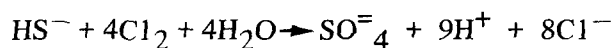
5.2.2 Chlorination

Chlorine is often applied in a trunk sewer, pump station, or headworks of a treatment plant. It acts both to destroy any sulfide present and to prevent sulfide buildup in the chlorinated wastewater for some time thereafter. It is sometimes used to prevent sulfide buildup in pressure mains where air injection is impractical or ineffective because of relative flatness of the main (11).

Calcium hypochlorite was occasionally used for the control of odors in solid and liquid wastes well over a century ago, and elemental chlorine has been used for this purpose since the 1920's (12). Chlorine and hypochlorite can be used interchangeably. Chlorine in dilute aqueous solution is in fact a mixture of hypochlorite and un-ionized hypochlorous acid. Sodium hypochlorite is used as a matter of convenience where the dosages are very small or occasional, but elemental chlorine is chosen as a matter of economy where larger amounts are needed. The term chlorination is to be understood as including the use of the hypochlorites. Concentrations and dosages of hypochlorites are expressed as the equivalent amount of chlorine.

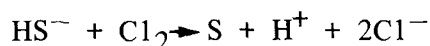
Chlorine reacts not only with sulfide but also with mercaptans, which are important odor components of wastewaters. The reaction of sulfide and mercaptans with chlorine is immediate, whereas biological deodorization with oxygen is slow. Chlorination does not remove odors as completely as does the slower biological oxidation, but most odor conditions attributable to wastewaters (but not sludges) are adequately controlled.

If an excess of chlorine is added to a wastewater containing sulfide, the sulfide is oxidized largely to sulfate according to the following reaction:



The reaction requires 8.87 parts by weight of chlorine for each part of sulfide (13). However, the chlorine reacts also with other constituents of the wastewater, so that 10 to 15 parts of chlorine may be consumed before the sulfur is converted completely to sulfate.

If chlorine is added slowly, with vigorous mixing, to a pure sulfide solution, the sulfide may be destroyed by being converted to sulfur according to the equation:



Chlorine consumption in this reaction is 2.22 parts by weight per part of sulfide. Other compounds, including thiosulfate, trithionate, and sulfite are produced when the degree of oxidation is intermediate between sulfur and sulfate.

In laboratory tests the chlorine requirement for elimination of sulfide in the wastewaters of the Los Angeles County Sanitation Districts was found to range from 3 to 9 times the sulfide concentration. Observations upstream and downstream from chlorination stations on the sewers showed somewhat larger requirements, probably because the mixing was less efficient than in the laboratory tests (14).

The addition of chlorine to a wastewater flow depresses biological activity in the stream, virtually stopping the consumption of oxygen until the chlorine residual has disappeared. During this period of suppressed biological activity the stream acquires an oxygen reserve that will delay the reappearance of sulfide downstream. The chlorine also leaves a residue of moderately active chlorine compounds that can destroy additional sulfide. These effects do not generally persist for more than about a half mile downstream unless excess dosages are applied. The use of excess dosages, however, is economically inefficient from the standpoint of over-all sulfide reduction.

Efficient use of the chlorine requires rapid and complete mixing of the chlorine solution with the wastewater stream, just as it does when chlorine is used for disinfection. The ideal method of application is for the wastewater and chlorine solution to come together in a small chamber in which enough energy is dissipated to complete the mixing in the minimum amount of time, preferably less than a second. Where a fall is available, this objective can usually be attained quite readily. By way of illustration, consider a wastewater stream entering the wet well of a pump station. One of the possible ways to accomplish rapid mixing would be to install a cubical or cylindrical open-top box under the inlet pipe, with a free fall into it and overflow out of it into the wet well. A free fall of a foot is suitable. The water level in the wet well should not rise higher than the top of the box. The box should provide a detention time generally in the range of 0.5 to 2 seconds. If the chlorine solution is added in this box, efficient mixing will be attained. The fall of one foot is satisfactory for any flow, small or large, but if the box is very large, the chlorine solution should be dispersed by way of a perforated plastic pipe.

Discharge of the chlorine solution into a hydraulic jump is another way to get good mixing.

In many cases there is not a practical way to get efficient mixing because of the variability of the wastewater composition and flow. Often there is little choice but to discharge the chlorine solution by way of a hose or a perforated plastic pipe into the stream in a sewer. If the stream is shallow, mixing is poor and local overdosing is likely to cause fuming. Poor mixing also results if the chlorine solution is discharged directly into a wet well.

Even with good mixing, there is no simple way to achieve the theoretically attainable chlorination efficiency when chlorinating a wastewater of variable flow and composition. In adjusting the dosage for chlorination of raw wastewater, tests of relevant characteristics of the water downstream are made. Chlorination may be carried to the point where a chlorine residual is shown by orthotolodine or other test reagent, or to the absence of sulfide, or perhaps to the elimination of sulfide at a relatively distant point downstream, as at the end of a pressure main. Often the chlorine application rate is programmed according to the time of the day after determining by trial what rates are necessary to attain the desired condition. The diurnal changes of rates may be made manually or by program timers. Sometimes the control is semiautomatic, wherein the chlorinator rate varies proportionally with wastewater flow, but with the proportion subject to manual or programmed control, or it may be fully automatic, wherein the dosage is controlled in response to signals from a downstream sensor. The sensor may make automatic colorimetric tests for chlorine residual or it may be an amperometric chlorine residual tester or an oxidation-reduction potential electrode. By use of a sulfide sensing electrode, it would be possible to control the chlorine dosage to the disappearance of dissolved sulfide, but as far as is known this had not been done.

Fully automatic control is not uncommon for the chlorination of treated wastewater effluents and for certain industrial wastes, notably for the destruction of cyanide, but it is doubtful practicability for upstream wastewater chlorination.

CASE HISTORY

In 1929 the newly installed regional trunk sewer system of the Los Angeles County Sanitation District (serving about a third of the area now served as shown in Figure 6-1) developed high sulfide concentrations as a result of sluggish flows in large, long trunks carrying only a few percent of their ultimate capacity. In 1931, eight chlorination stations were established on upstream tributary trunks, whereby satisfactory sulfide control was attained (15). In 1939, when the flow was 24 mgd, or about 2½ times as great as in 1931, an assessment of the chlorination program was made. With the chlorinators turned off, the dissolved sulfide concentrations entering the downstream treatment plant averaged 1.05 mg/l. With applied chlorine equivalent to 12 mg/l in the total wastewater flow, dissolved sulfide concentrations averaged 0.43 mg/l. Thus the ratio of chlorine applied to sulfide eliminated was 19 to 1. The poor ratio was due mostly to the necessary overdosing at the upstream locations. The wastewater flow carried by the system increased rapidly in subsequent years, and the chlorination program was gradually phased out.

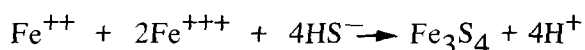
5.2.3 Metallic Salts

The salts of many metals will react with dissolved sulfide to precipitate insoluble sulfides, and thereby prevent the escape of H_2S to the atmosphere. Insolubility is a matter of degree. For this method to be fully effective, the metal sulfide formed must be highly insoluble. The use of these salts must be considered in the light of possible effects on treatment processes and effluent quality.

5.2.3.1 Iron Salts

One metal that has been used in this way is iron. There are several iron sulfides that may form: pyrrhotite, varying in composition from FeS to Fe_4S_5 ; ferric sulfide, Fe_2S_3 ; smythite, Fe_3S_4 ; and pyrite and marcasite, both having the formula FeS_2 . FeS_2 is found among the corrosion products on iron that has corroded in the presence of sulfide, and it is found in sewers where iron concentrations are high. It is probably formed by oxidation of other iron sulfides.

Neither pyrrhotite nor ferric sulfide alone is sufficiently insoluble to lower the dissolved sulfide content below several tenths of a milligram per liter. If a mixture of ferrous and ferric salts is added to a sulfide-containing wastewater, better results are obtained than with either one alone. The optimum mixture is one with a molecular ratio of one part of ferrous to two parts of ferric (14). The dissolved sulfide concentration can be reduced to 0.2 mg/l with only a moderate excess of iron. Presumably this reaction is as shown below:



The combination of a small amount of dissolved oxygen along with a ferrous salt also reduces dissolved sulfide to low levels.

Freshly precipitated iron sulfides are readily oxidized by oxygen, producing sulfur. Thus, while oxygen promotes the precipitation of iron sulfides, iron acts as a catalyst to promote the oxidation of sulfide.

If an excess of iron, ferrous or ferric, is added to a sample of wastewater which is then incubated in the absence of air so that high sulfide concentrations are produced, the dissolved sulfide concentration will rise to about 2 mg/l. Similarly, concentrations of 1 to 2 mg/l of dissolved sulfide were found in a sewer to which a large excess of iron had been added (14). Presumably the iron becomes tightly bound to other radicals, which may include organic matter, orthophosphate, polyphosphate, and other chelates added in cleaning compounds. However, there are cases where the presence of iron seems to hold dissolved sulfide to a few tenths of a mg/l. The difference may be related to the amount of dissolved oxygen in the wastewater.

Iron salts are occasionally added to industrial wastes of high sulfide content, provided the reduction of dissolved sulfide to 1 mg/l is satisfactory. Furthermore, the addition of ferrous chloride to anaerobic sludge digestion tanks plagued with high sulfide concentrations has caused spectacular improvement of the digestion process.

5.2.3.2 Zinc Salts

Zinc sulfide is much less soluble than iron sulfide. The addition of a zinc salt to sulfide-containing sewage generally reduces the dissolved sulfide concentrations to less than 0.1 mg/l. No large excess of zinc is required.

Because of the strong affinity of zinc for sulfide, it was hoped that an excess of zinc added at an upstream point would assure freedom from H_2S downstream. Results have been disappointing. As in the case of iron, the zinc appears to become bound in other combinations, so that the objective is not attained except by use of large excesses of zinc.

At one time zinc was applied in rather large amounts to a large trunk sewer of the City of Los Angeles, using a solution prepared by dissolving scrap zinc in waste acids, but the operation has been discontinued. It is still used in some instances for treating small industrial wastewater flows.

5.2.3.3 Other Metals

Lead sulfide, PbS , is much less soluble than ZnS , but the application of lead salts for this purpose would be uneconomical, and the increased lead content of the sludge might be objectional. The silver and copper sulfides, Ag_2S , Cu_2S , and CuS , are so extremely insoluble that they do not react in the analytical tests for sulfide. Copper is present in small amounts in ordinary wastewaters, normally in concentrations of the order of 0.1 mg/l, or more where copper plumbing is used. Thus a very small part of the sulfide in wastewaters may be combined with copper, but there is no easy way of determining this. Sulfide thus bound is for practical purposes nonexistent. Copper salts would probably be very effective for sulfide control, but the cost would be very high, and if an excess of copper were used it probably would have harmful effects on aerobic wastewater treatment processes.

5.2.4 Nitrate

Certain bacteria can oxidize organic matter by reducing the nitrate radical. The nitrogen is converted principally to N_2 . The addition of nitrate to a sewer does not directly affect the oxygen balance, because nitrate reduction does not occur in the presence of oxygen. Sulfate reduction does not occur in the presence of nitrate if nitrate-reducing bacteria are present.

Nitrate may serve to prevent sulfide buildup by preventing sulfate reduction, and nitrate-reducing bacteria can use nitrate to oxidize sulfide if oxygen is not available. A small amount of nitrate in a wastewater stream may not prevent sulfate reduction in the slime layer where nitrate as well as oxygen may be entirely depleted.

Nitrate has been used in some places for sulfide control in sewers, being added either as calcium nitrate or sodium nitrate. It may have relatively little effect when first added, because of a scarcity of nitrate-reducing bacteria. A population of these bacteria develops in the slime layer, so the reaction is more rapid after a day or two of treatment. Since the reaction occurs mostly in the slime layer, where organic matter is abundant, much of the nitrate is consumed in oxidizing organic matter. The amount of nitrate required to destroy sulfide in a sewer may be estimated as 10 pounds of NaNO_3 per pound of sulfide if sulfide concentrations are high. The ratio may be 20 to 30 when the sulfide concentrations are low, and will be even larger if the nitrate is added at the upper end of a trunk as a preventive.

Nitrate is more effective when used for the chemical control of sulfide in overloaded oxidation ponds, presumably because the long residence time allows the development of a culture of nitrate reducers in the water.

To treat an oxidation pond, the nitrate salt is first dissolved in water. It may be dispersed into the water in the pond by adding it continually to a stream flowing into the pond or into a recirculating stream, or by spraying the solution onto the surface of the pond.

CASE HISTORY

In 1958 the Davis Cannery at Atwater, California, was discharging 0.74 mgd of wastewater from the canning of peaches, with a BOD concentration averaging 300 mg/l, or a total of 1,850 lb/day of 5-day of BOD. The wastewater went to ponds with a surface area of 5.84 acres. High sulfide concentrations developed. Application of 1,000 lb/day of NaNO_3 to the water leaving the cannery reduced total sulfide concentrations in the ponds to zero in the daytime, with a maximum of 0.3 mg/l in the early morning.

5.2.5 pH Control and the Use of Strong Alkalies

Since the proportion of dissolved sulfide existing as H_2S diminishes rapidly as the pH is increased, it follows that problems due to escaping H_2S can be diminished by adding alkalies. Slaked lime has been used experimentally for this purpose, but the method has not proved useful. Rather large dosages are needed, probably 50 mg/l or more in a typical case, if H_2S is to be reduced to acceptable levels in the presence of moderately high sulfide levels. A dosage of 25 mg/l might suffice for low sulfide concentrations, but chlorine might then be more satisfactory.

The attempt to control H_2S by controlling pH has the shortcoming that if the amount of sulfide in solution remains unchanged, the problem of H_2S in the air may recur from any circumstance that lowers the pH again. The treatment is not useful, for instance, at the

upper-end of a long trunk, because the pH will be lowered by tributary flows and by the production of CO_2 and organic acids through biological action, which will not be substantially impeded as long as the pH is below 9. The attempt to apply lime continuously at the upper end of a trunk in sufficient amount to be effective all the way down the line would be impractical, because the upstream part of the trunk would accumulate an incrustation of calcium carbonate.

It is desirable, from several points of view, to keep the pH of wastewater as high as is practical by proper regulation of industrial waste discharges. The policy of the Los Angeles County Sanitation Districts, for example, in respect to pH control has been strict exclusion of acids, with a minimum allowable pH of 6.0 in wastewaters discharged to the sewers, and encouragement of the discharge of high pH wastes. Thus, industries that were producing acetylene from calcium carbide were invited to run their spent lime into the sewer, and various spent solutions of caustic soda were also welcomed if they did not have objectional characteristics such as strong odor or high oil content.

An upper limit for the pH established in many sewer-use regulations is not based upon a realistic appraisal of the effects. The neutralization of high-pH wastes before discharge to the sewer is usually detrimental. The lower the pH, the less buffer there is against serious effects of accidental acid discharges. High pH, on the other hand, diminishes corrosion and odors, and rarely has any undesirable effects. In some instances, continuous discharges to small sewers of high-pH wastes, as for example from bottle-washing operations, have caused incrustations in the sewers. These problems have been resolved by requiring inpoundment of the wastes with periodic slug discharges, perhaps once each day, or as often as once an hour.

Excessive discharges of strong alkalis can, of course, raise the pH to unacceptable levels in treatment plants. If the pH in a biological oxidation process is higher than 9, the efficiency may be substantially impaired, and it may be virtually stopped at a pH of 10. The buffer capacity of wastewater, and especially of activated sludge tanks, is high enough so that it takes rather large amounts of strong alkalis to raise the pH to harmful levels.

Beyond serving to maintain higher pH values, alkalies have an important application as sterilizing agents if they are added at high concentration. Sulfide generation in a sewer can be stopped if the slime layer is inactivated, and it takes several days for it to return to normal. This effect has been shown with strong alkalies, strong acids, and chlorine. The use of chlorine for this purpose is quite expensive, although where a station for in-sewer chlorination exists, suppression of slime activity for some distance downstream is observed. Acid is undesirable for the reasons previously mentioned.

Both slaked lime and quicklime have proved practical for inactivating the slime. The lime is ordinarily poured by hand into a manhole at a rate that gives a dosage between 5,000 and 10,000 mg/l for a period of about 20 minutes. In other cases, caustic soda solutions have been used, discharging from a tank truck directly to the sewer. The length of time for a

sewer to regain its sulfide-generating capability varies with the temperature and with the intensity of the chemical treatment. If alkalies are used in a sufficiently high concentration, it is possible to approach the condition of 100 percent sterilization of the slime layer, but this may not be optimal from the standpoint of economy. If the pH during in-line chemical treatment is raised to 12, sulfide generation in the summer may return to $\frac{1}{2}$ the normal rate within a week. In one case it reached normal levels in three days. If the pH is raised to 13, there is likely to be very little sulfide generation for a week, but it will return to near normal within two weeks. More intensive treatment does not extend this time any further. The chemical dosage to reach pH 13 is very high, so the optimal treatment may be pH 12.5 or somewhat higher at weekly intervals during the summer, and at two-week intervals during the winter. The actual schedule to be followed in any particular application will be determined by local conditions (1).

CASE HISTORY

Sodium hydroxide is the principal chemical now used for sulfide control by the Los Angeles County Sanitation Districts. It is used at local trouble spots, usually in flows less than 3 cfs. Waste caustic solution from industries, generally quite dilute, is used to the extent available, and concentrated commercial caustic is purchased when necessary. In either case, it is applied from a tank truck. The duration of a treatment is 20 minutes, and the objective is a pH of 12.5. Required frequency of treatment is determined by a routine testing program.

The scope of this operation is indicated by the records for August, 1973, which show that about 70,000 lb of NaOH were used in that month for treating 25 lines, mostly gravity sewers but including some force mains. There is no noticeable effect on the pH at the main treatment plant, and it is not likely that there is more than a very small effect there on the average sulfide concentration, since none of the major trunks are treated.

The amounts used in the winter are very small.

5.2.6 Hydrogen Peroxide

Hydrogen peroxide is another chemical that has and is being used to control hydrogen sulfide in wastewater. Data has been presented to show that hydrogen peroxide reacts with hydrogen sulfide to form water and sulfur (17). Theoretically, this reaction requires a 1:1 ratio of hydrogen peroxide to hydrogen sulfide. In practice, however, a higher ratio is employed (as shown by the following case histories). This results in a contribution of dissolved oxygen which inhibits the regeneration of hydrogen sulfide.

Installations where hydrogen peroxide has or is being applied for the purpose of controlling hydrogen sulfide in wastewater include: Ocala, Florida; Ft. Lauderdale, Florida; Hollywood, Florida; Sunrise City, Florida; Dade County, Florida; Broward County, Florida; Hampton Roads, Virginia; Corpus Christi, Texas; Ft. Worth, Texas; and Bluff Cove, California. The following case histories present some of the data collected at two of these installations.

CASE HISTORY I

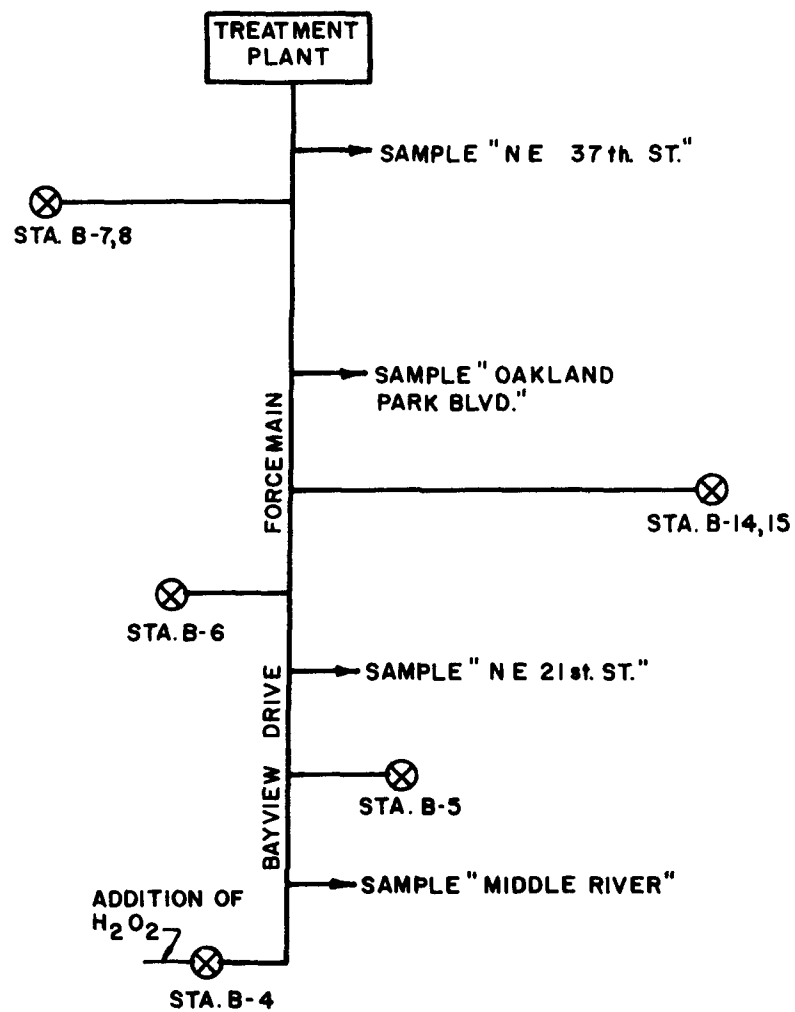
Figure 5-9 shows schematically the Bayview Drive force main in the Ft. Lauderdale, Florida, wastewater system. The main is about 3 miles long, made of 14", 16", and 18" pipe. It receives four pumped flows.

It is reported (16) that applications of hydrogen peroxide at pump station B-4 gave results as shown in Table 5-4. The dosages are expressed as ratios of peroxide added to quantity of sulfide carried by the flow into station B-4. The tests were made over a 12-day period, but the results are grouped by the hour of the day.

TABLE 5-4
HYDROGEN PEROXIDE TREATMENTS AT FT. LAUDERDALE, FLORIDA

Hour	Ratio of hydrogen peroxide to sul- fide at Stn. B-4	Total Sulfide Found, mg/l				
		Stn B-4	Middle River	NE 21st St	Oakland Park Blvd	NE 37th St
9-10 AM	0	3	4	7	6	5
	2:1	0.1	0	0	3	5
	3:1	0	0	0	1.1	1.5
	4:1	0	0	0	0	0
10-11 AM	2:1	0.2	0	0	1.5	3
	3:1	0.1	0	0	0.9	3
	4:1	0.1	0	0	1.0	1.8
1-2 PM	2:1	0.2	0	0	2	4
	3:1	0.2	0	0	1.4	3
	4:1	0.1	0	0	0.8	2
2-3 PM	0	3	3	6	6	6
	2:1	0.1	0	0	3	2
3-4 PM	2:1	0.1	0	0	3	3
	3:1	0.1	0	0	1.2	3
	4:1	0	0	0	0	2

FIGURE 5-9
BAYVIEW DRIVE FORCE MAIN
FT. LAUDERDALE SYSTEM



CASE HISTORY II

Hydrogen peroxide was added at Bluff Cove pump station of Los Angeles County Sanitation Districts (1). The pumps discharge into a pressure main 12 inches in diameter and 1,965 feet long. Pumping is intermittent; the average retention time is about two hours. Various dosages of hydrogen peroxide were added. The solution feed pump was electrically connected to the wastewater pump, so that at any fixed feeding rate all of the wastewater received the same dosage. Sulfide tests were made at the pump station and at the end of the force main, with results as shown in the following table. Three qualitative tests for peroxide at the end of the force main were negative.

TABLE 5-5
EFFECT OF HYDROGEN PEROXIDE IN BLUFF COVE FORCE MAIN

Date	H ₂ O ₂ * feed rate, mg/l	Waste- water Temp., °C	Total Sulfide				Dissolved Oxygen, End Force Main, mg/l
			Pump Station		End Force Main		
			No. Tests	Avg. mg/l	No. Tests	Avg. mg/l	
16 Sept	0	27.0			9	6.1	
21 Sept	0	26.1			12	6.4	
22 Sept	27	26.2			8	2.1	
23 Sept	27	26.4	8	1.2	8	2.1	2.2
25 Sept	27	26.1	11	0.8	9	1.5	1.2
1 Oct	32	26.0			4	0.4	8
2 Oct	32	25.8	8	1.0	8	0.8	8
2 Oct	0**				8	4.5	
7 Oct	15***	25.6			7	0.35	16
9 Oct	41	24.7			8	0.66	4

*The feed rate is expressed in terms of actual weight of H₂O₂, not the weight of a commercial solution.

**Immediately after cessation of the H₂O₂ treatment.

***This recorded dosage is evidently erroneous. See text.

Comparing the results of September 16 to 25, it appears that 27 mg/l of H₂O₂ eliminated about 4.4 mg/l of sulfide but leaving a substantial sulfide residual. Comparing the results of October 1 and 2, 32 mg/l of H₂O₂ eliminated 3.9 mg/l of sulfide, lowering the total sulfide concentration to where little other than insoluble metallic sulfides remained. The result for October 7 looks very good since only 15 mg/l apparently reduced sulfide to a satisfactory level, but the finding of 16 mg/l of dissolved oxygen at the end of the force main shows that the recorded dosage of 15 mg/l must be in error.

An experiment was made to determine if continuous peroxide application would affect the regeneration of a slime layer that had been destroyed by caustic treatment. The Bluff Cove force main was treated with NaOH and NaOCl, after which there was no sulfide

generation. It required 16 days for generation to return to normal. The treatment was repeated and then peroxide was fed continuously, except for 24 hours on the fifth and sixth days, at a dosage rate of 12 to 22 mg/l. The slime layer returned to normal within a day or two of the time required when no peroxide was used.

5.2.7 Other Chemicals

There are other possible oxidizing agents that could be used for sulfide control. Some of them, such as chlorate and chromate, react biologically. Others, including permanganate and ozone, destroy sulfide chemically.

At one time waste chromate solution was trucked from a large plating works to a point where it was put into tanks and fed into a trunk sewer at a rate adjusted to eliminate sulfide for a considerable distance downstream. The chromium was rendered insoluble and harmless as a result of its reduction to the trivalent form.

Permanganate has sometimes been used for treating sulfide-containing well waters, but not for the sole purpose of destroying sulfide. Ozone has been tried a number of times for sulfide control in wastewaters. It is necessary to bring the ozonized air into contact with the wastewater to dissolve ozone. In this operation, much more oxygen dissolves than ozone, and since oxygen reacts with sulfide, the prior ozonizing of the air is unnecessary (14).

Ozone is effective for deodorizing sewer air but an excess of ozone must be avoided, since it can be an objectionable as the original pollutants.

5.3 Control of Industrial Wastes

The desirability of strict limitation of low-pH discharges to the sewers and the advantage of high-pH wastes were discussed in Section 5.2.4. In addition to a prohibition against acid discharges, secure measures must be prescribed to assure that spills do not occur.

In one treatment plant where the flow was 16 mgd, the wastewater suddenly became so acid that the pH dropped to about 2, and H_2S in the wastewater, arising from the dissolving of iron sulfide in the slimes, reached 80 mg/l. Ordinarily H_2S concentrations there were not high enough to be of concern. Several years later there was an apparent recurrence of that incident. Two men working in the trunk sewer at that time were killed by the high H_2S concentrations. Even where a sewer carries wastewater with little or no sulfide, iron sulfide is generally present in the slimes in sufficient amount to produce high concentrations of H_2S when strong acid is discharged.

To assure against discharges of acids or other harmful chemicals to the sewer, it is sometimes necessary to require a retention tank large enough to hold an amount of the industrial wastewater equal to a 24-hr flow. The tank should be kept mixed, with the wastewater

flowing through and overflowing to the sewer, with no way to dump it to the sewer. Where large amounts of acid are stored, there must be provisions, such as diked areas, to hold spills.

Sulfide-containing industrial wastes should be controlled or excluded from the sewers if a low sulfide system is to be maintained. Sulfide-containing wastes may be produced by tanneries, petroleum refineries, paper pulp mills, and a variety of other chemical industries. Sometimes a municipality has established a policy of accepting such wastes on the basis that the system was built for that purpose, or that a central treatment works can do the job more economically than can a number of individual plants. This policy has the potential disadvantage of possible lethal atmospheres and corrosion in manholes and in sewers if they are corrodable, and odors from the sewers and at the wastewater treatment plant. The problems at the treatment plant can be dealt with by proper procedures, but in view of the erratic nature of industrial discharges, it would be difficult to regulate a treatment process on the sewerage system so as to maintain a low sulfide condition in the sewers. It is usually better that the waste be treated at the source.

As an example, a small tannery that was discharging spent depilatory to the sewer was told that the discharge was unacceptable. The procedure then adopted was to collect the wastes in a tank equipped with a stirrer, where they were treated batchwise with an excess of ferrous sulfate solution. Precipitation of ferrous sulfide reduced dissolved sulfide to 1.0 mg/l or less, after which the mixture was discharged to the sewer.

The concentration of 1 mg/l of dissolved sulfide allowed in this example was a special action based upon a consideration of the dilution available in the trunk sewer and the limitations of the method employed for precipitating dissolved sulfide. In cities where sewer use ordinances include restrictions of sulfide-containing wastes, the limit is usually placed at 0.1 mg/l of dissolved sulfide.

It may be necessary to control industrial wastewaters that act to accelerate sulfide generation. Two factors are involved, temperature and nutrient concentration. High temperature in a sewer is undesirable for a number of reasons, including thermal stresses affecting the pipe, fog in the sewer atmosphere interfering with maintenance operations, fog issuing from manholes, and an increase of the rate of use of oxygen and of production of sulfide.

A regulation commonly used places an upper limit of 120 deg F (49 deg C) on the temperature of wastes acceptable into the sewers. This does not imply that 120 deg F would be a satisfactory condition in sewers, but recognizes that, in view of the available dilution, it would seldom be worthwhile to require an industry to provide facilities to cool a water below that temperature.

Where a special problem is created, as for example a large flow of water near 120 deg F is discharged into a relatively small sewer, remedies may be called for under the general clause of an ordinance categorically prohibiting harmful discharges.

The rate at which a slime layer can produce sulfide is proportional to the concentration of certain organic nutrients, unless sulfate is in short supply, in which case the rate may depend only upon the sulfate concentration, or upon both the sulfate and organic nutrient concentrations. Rarely are specific limitations placed upon sulfate unless the concentrations are so high that there are other problems as well, such as excessive mineralization of effluents or interference with anaerobic digester operation.

No way is known to measure the concentrations of nutrients used by sulfide-producing bacteria in the slime layer of a sewer, since almost nothing is known about the identity of these nutrients. In domestic-type wastewaters, there appears to be a general proportionality between the sulfide-active nutrients and BOD. BOD will continue to be used as a measure of such nutrients until some new basis is found. BOD is significant as a measure of the load on biological oxidation processes, and this is one of the reasons that limits are placed on the BOD of wastes received into sewers, or that BOD is one of the parameters for charges for sewer service. In this situation, the effect of BOD on sulfide generation is a minor consideration.

Where a wastewater is not subjected to biological oxidation, BOD limitations may be advisable for reasons of sulfide generation, but it may be necessary to establish a correlation between sulfide generation and the BOD or COD of a waste.

In 1948-51, the City of Newport Beach, California, had to continue to use an overloaded system, including a primary treatment plant, pending the construction of the Orange County Sanitation Districts joint facilities. Pumping capacity in particular was overloaded, and the wastewater backed up in the trunk sewers, leading to sulfide concentrations in the summer averaging 6 mg/l. In the autumn, three fish canneries operated, boosting sulfide to even higher levels. It was necessary to disinfect the effluent by chlorination, and to use primary effluent for the chlorine solution water, which is wasteful because of its high breakpoint chlorine demand. The required dosage was at times 120 mg/l.

When the fish canneries were operating, the total BOD load in the wastewater averaged 2,000 lb/day, of which 1,200 lb were due to the canneries. Sulfide buildup varied linearly with EBOD in the domestic sewage, but the BOD of the fish cannery waste was only 25 percent as effective in stimulating sulfide generation. The increment of cost to the City for the chlorination of sulfide due to the fish cannery operation was charged to the three companies in proportion to the tonnage of fish that each had processed.

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CHAPTER 6

DESIGNING TO AVOID SULFIDE PROBLEMS

6.1 Basic Concept

Severe sulfide problems arise in sewerage systems where flows are sluggish or the wastewater is contained for some time in filled pipes out of contact with air. There is practically no buildup in partly filled small sewers flowing at a velocity of 2 ft/sec or more. In large trunks, buildup does occur even at considerably higher velocities, but then the rate of buildup is slow, rarely producing concentrations higher than 1 mg/l.

A gravity sewer at good velocity may, of course, show high concentrations if sulfide is contributed by upstream pipes that are completely filled or that are carrying wastewater at sluggish velocities.

In any case, the sulfide concentrations that are found in sewers are closely related to the design of the system. Severe sulfide conditions, with concentrations above 1 mg/l, should be avoided by proper design, and the lower concentrations that are common in large trunks should be minimized or eliminated by proper treatment or should be taken into account by planning facilities that will avoid odor problems and corrosion.

Many of the measures suggested to solve existing sulfide problems, such as air injection into force mains, in-line aeration, and others, should be considered at the time that a system is designed. Since they have already been discussed in Chapter 5, this section will deal with the major design features that are of an irrevocable nature.

6.2 Slopes of Small Collecting Sewers

Figure 3-12 shows the effect of slope on sulfide buildup in collecting sewers in residential areas.

It might appear that the rate of sulfide buildup shown by line B of that figure, for slopes averaging 0.4 percent, would not be too bad, but the production of about 0.25 mg/l of sulfide in the first ¼ mile of flow is not consistent with an intent to build a system free of sulfide problems. Furthermore, the figure does not tell the whole story, since it shows only average results.

Table 6-1 shows the average sulfide concentrations for the highest 5 percent and 10 percent of the sulfide concentration results for the sewers represented in the figure. Maximum sulfide concentrations are also shown.

TABLE 6-1

SULFIDE CONCENTRATIONS IN SMALL COLLECTING SEWERS

Line (Fig. 3-12)	Average slope percent	Number of results	Sulfide Concentrations		
			Average of highest 10% mg/l	Average of highest 5% mg/l	Maximum mg/l
A	0.23	133	1.44	1.8	2.8
B	0.40	147	0.93	1.35	2.0
C	0.57	141	0.41	0.49	0.6
D	0.9	46	0.13		0.2

The City of Long Beach, California, has had for many years an exceptionally efficient sewer maintenance program (1). The City has found that small sewers at a slope of 0.4 percent should in general be cleaned annually with a ball or other hydraulic device, but that where the slope is 0.6 percent, it is sufficient to ball the lines once in five years, and then mostly as a precautionary measure.

The sewer ordinances in some cities now have this provision: "The standard minimum slope shall be 0.006 (0.6 percent) except where the sewer will serve more than 400 connections. Slopes less than the standard minimum slopes may be used only if justified in an engineering report, approved by the City Manager, showing that it is not practical to attain the standard slopes."

This seems like a reasonable provision, except that in the light of information now available it might be permissible to allow a flatter slope after 100 connections instead of 400. It may be added that when the engineering report called for in the ordinance is reviewed, any allowed exceptions to the 0.6 percent standard should be limited to short distances, and an exception should in no case allow a slope less than 0.4 percent.

There are areas where small sewers have been laid at slopes much flatter than the standards here recommended, and yet they have operated with no sulfide generation. This was found to be the case, for example, in a city near the Gulf of Mexico coast. The required slope of the upper ends of the sewers is 0.33 percent, decreasing to flatter slopes after a short distance. An examination of the system showed that 75 percent of the flow in the sewers was infiltrated groundwater, which increased the oxygen supply and diluted the oxygen-demanding components. Even pressure mains produced very little sulfide. Similar conditions exist in many flat areas with high groundwater levels.

It is now required that sewers be laid with tight joints (2). This may require revision of previous slope or velocity standards to prevent serious sulfide problems. One city that continued to lay small sewers at a slope of 0.2 percent, but with tighter joints than in the past, has experienced many odor complaints, liability actions for corrosion of plumbing on account of H_2S from the sewer, serious damage to a pump station, collapse of trunk sewers, and the loss of two lives due to hydrogen sulfide poisoning. The difficulties were caused partly by sulfide produced in pressure mains, but were mostly due to buildup in the flat collecting sewers.

The sewers represented in Figure 3-12 were in dry areas where there was little or no infiltration. They indicate what may be expected in other areas where temperatures are similar and tight joints are used. Lower temperatures might permit slightly flatter slopes. However, velocities in the small sewers are considerably less than 2 ft/sec even at a slope of 0.6 percent. Any lessening of the slope will augment the concentrating of organic solids along the bottom of the channel and intermittent ponding of the water, producing sulfide at a rate influenced much more by the deposition of solids than by the temperature.

6.3 Slopes of Larger Sewers

Figure 3-13 and the explanation following it was prepared on the basis of all of the data now available to show what may be expected when certain slope-flow relationships prevail. Thus, if the average rates of elevation loss are in general below Curve B of Figure 3-13, sulfide generation will be at such a level that supplemental aeration or some chemical control method may be considered necessary, and corrosion-resistant structures will generally be called for. Use of average slopes that are between Curves A and B will be expected to lead to moderate sulfide concentrations which may cause odor and excessive corrosion problems at points of turbulence. If the slopes are above Curve A, sulfide is expected to be negligible.

The slopes shown in Figure 3-13 apply where the daytime EBOD in the summer, or climactic EBOD, is 500 mg/l. The slopes should be increased or decreased in proportion to the square root of the climactic EBOD.

It must be observed that the scale of rates of elevation loss does not mean the actual slopes of uniform reaches, but the total elevation loss (or, more strictly, energy loss) divided by distance. Distance traveled by the wastewater in one-hour intervals can be used in determining average energy gradients.

Reasonable judgment must be used in applying Figure 3-13. Even if the desired *average* energy gradient is attained, the velocity should *nowhere* be less than 1.5 ft/sec under daily peak flow conditions, and preferably 2.0 ft/sec, lest sulfide be produced in amounts that will cause trouble in subsequent steeper sections. It must also be remembered that an upstream sulfide producer such as a pressure main can yield sulfide concentrations that may persist for a rather long distance downstream.

The slopes that should actually be used in a given situation will depend upon objectives and upon many factors other than flow and EBOD. Consideration needs to be given to odor problems, kind and size of the pipe, economics, effects of "septic" wastewater on treatment plant operation, etc. If the sewage is to be pumped, a saving of pumping head should never, by itself, be a reason for using slopes that will cause significant sulfide buildup. The energy dissipated by the stream as it loses elevation accomplishes some degree of oxidation. Thus, more energy spent for pumping will result in a smaller power requirement at the biological oxidation plant. Where good slopes prevail, the amount of in-sewer oxidation may be substantial (3). However, where the attainment of slopes corresponding to Curve A would mean multiplying the number of pump stations excessively, or would require extremely expensive sewer construction deep in water-saturated soil, it may be necessary to settle for less. Suitable procedures will then be called for to prevent odor and corrosion problems.

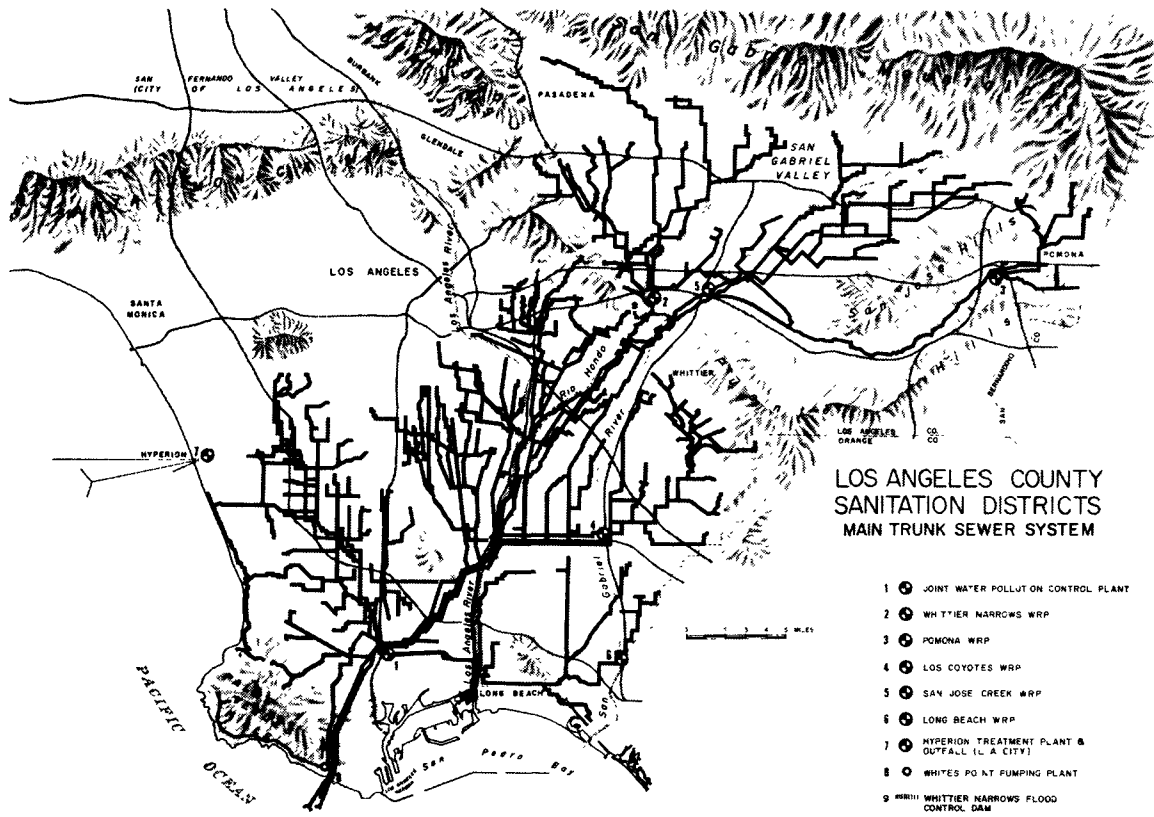
CASE HISTORY

The Los Angeles County Sanitation Districts constitute a joint venture of 27 districts to provide solid and liquid waste disposal facilities for a population of 4.0 million persons in an area of 724 sq mi. Except for ten detached districts, the service area lies generally south to northeast of the City of Los Angeles. A major part of the industrial area of Los Angeles County lies in the Sanitation Districts. The Districts operate 1,050 miles of trunk sewer, to which are connected nearly 8,000 miles of smaller sewers owned by 71 cities plus other local agencies.

Seventeen contiguous districts, including 96 percent of the total population, operate the main trunk sewer system shown in Figure 6-1. Many of the lines shown in the figure represent 2 or 3 parallel trunks, necessitated by large expansions of the original service area and intensive development. This system is connected to the Joint Water Pollution Control Plant (JWPCP), where the collected wastewater is treated before discharge by way of tunnels and outfalls to the ocean. However, six upstream water reclamation plants withdraw wastewater from the trunk sewers for local treatment, with return of sludge to the trunks. About 380 mgd, or 85 percent of the total flow generated in the main system, reaches the JWPCP.

During the first years of operation of the system, large trunks carrying flows as small as one percent of the design capacity were the site of severe sulfide problems (4). Eight chlorination stations were installed on the trunk sewers and were operated for several years, until no longer needed. On the basis of research done by the Districts (5), design standards were adopted which in general called for slopes that would produce velocities of 3 ft/sec in the trunk sewers. The Districts have continued to use this standard with satisfactory results. Occasionally sewers were laid at flatter slopes; objectionable sulfide generation has often resulted in these cases. Thus, the standard that was adopted has been successful, even though rather crude in the light of the more extensive information now available.

FIGURE 6-1
LACSD MAIN TRUNK SEWER SYSTEM



The topography in the upper parts of the system, especially in the San Gabriel Valley, provides fall well in excess of the requirements of Curve A of Figure 3-13. Figure 6-2 shows profile of the land surface along the routes of trunk sewers to the foothills north of Pasadena and to the eastern end of the system at Claremont. There are local areas in the San Gabriel Valley where inadequate slopes allow significant sulfide buildup, but the total oxygen resources of the upper part of the system are such that dissolved sulfide concentrations in the major trunks leaving the Valley by way of Whittier Narrows are zero.

Over much of the coastal plain the topography is less favorable, and the options for sewer routing do not allow full benefit to be taken of the natural slopes. Approaching JWPCP, the terrain is quite flat. The average condition of the major part of the system below Whittier Narrows can be described as intermediate between Curves A and B of Figure 3-13, but for a distance of about 8 mi upstream from JWPCP it is below Curve B. The annual average total sulfide concentration reaching JWPCP is 0.66 mg/l. The figure would be a few hundredths of a mg/l higher if it were not for chemical sulfide control in local trouble spots, as described in Chapter 5. Dissolved sulfide is only 0.2 to 0.3 mg/l at JWPCP. It is believed that the high iron content of the wastewater helps to keep dissolved sulfide to this low level.

The City of Long Beach and other areas along the coast gain access to the system by pumping.

The Los Angeles system, serving the City of Los Angeles and several adjacent cities, is similar to the County system, and the physiography of the area served is similar. The annual average dissolved sulfide concentration at Hyperion is 0.3 to 0.4 mg/l. Most of this sulfide content is produced in the last few miles upstream from Hyperion.

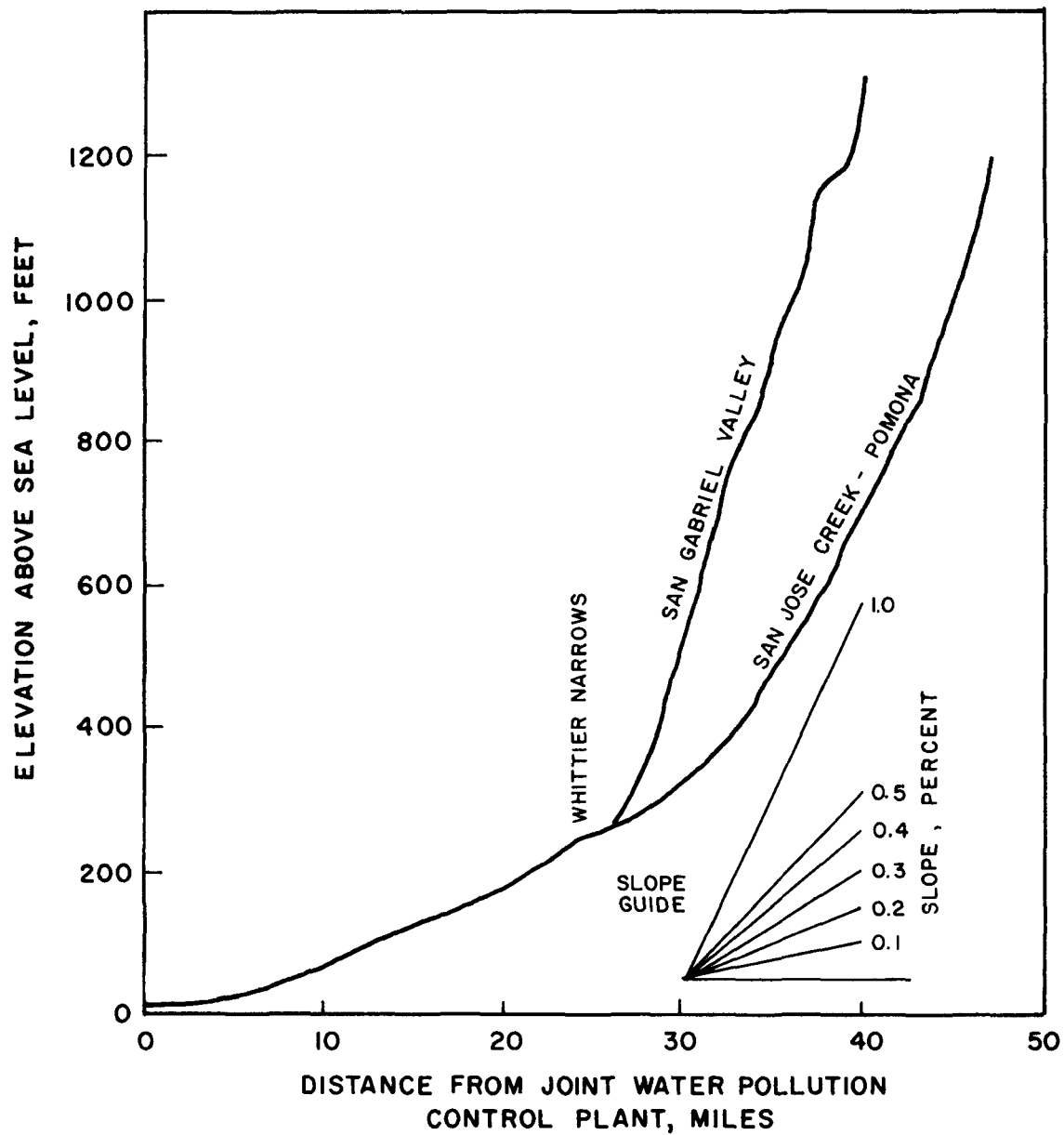
6.4 Sewer Sizes

If pipe size is decreased, slope and flow remaining the same, the velocity is virtually unchanged (6), but mean hydraulic depth (area of the cross section of the stream divided by surface width) is increased, and hence the reaeration rate of the stream is diminished. The effect is not large as long as the pipe is less than half full. When the pipe is nearly full, the mean hydraulic depth increases rapidly, seriously diminishing the oxygen supply. For the same quantity of wastewater and slope, the largest practical pipe size is the best if sulfide generation is determined to be a problem.

6.5 Points of Turbulence

A condition of excessive turbulence that mixes air with the wastewater results in a substantial input of dissolved oxygen. At the same time, it results in a corresponding increase in the rate of release of H_2S , if any is present in the wastewater, as well as the release of other odors. If a wastewater stream does not contain H_2S , and if the other odors do not cause a problem, turbulence is advantageous. Much more oxygen is dissolved in a fall than

FIGURE 6-2
GENERAL PROFILES OF PORTIONS OF LOS ANGELES
COUNTY SANITATION DISTRICTS SYSTEM



during the same loss of elevation in smooth flow. If a wastewater flow makes an abrupt fall of one foot, it will generally dissolve more oxygen there than it will in a half mile of flow at a slope of 0.1 percent.

In any real system, points of turbulence are unavoidable, and in the large trunk sewers sulfide concentrations of a few tenths of a mg/l are common. Therefore there may be corrosion of manholes and unprotected concrete pipe, and there may be significant release of H_2S into the atmosphere.

The best way to deal with the odor problem is to design structures in such a way that the released odors are confined. Normally air moves downstream in the sewer. If there is to be a hydraulic jump, it should be (and usually is) in the pipe downstream from the manhole. A major junction may be constructed within a vault or chamber entered by a manhole at its upstream end and so designed that air that has been exposed to the high turbulence of the junction will be carried downstream and not exhaled from the manhole. If the wastewater will carry sulfide, the junction structure will probably need to be protected by a lining, and the pipe, too, will need to be protected or of non-corrodable material. The distance downstream that abnormal sulfide concentration will prevail will depend upon the turbulence of the air stream, its velocity, size of the pipe, and perhaps some other factors. The H_2S concentration of the air will probably be near a steady state value at a distance downstream from the point of turbulence equal to 100 to 200 times the pipe diameter.

6.6 Pump Stations and Force Mains

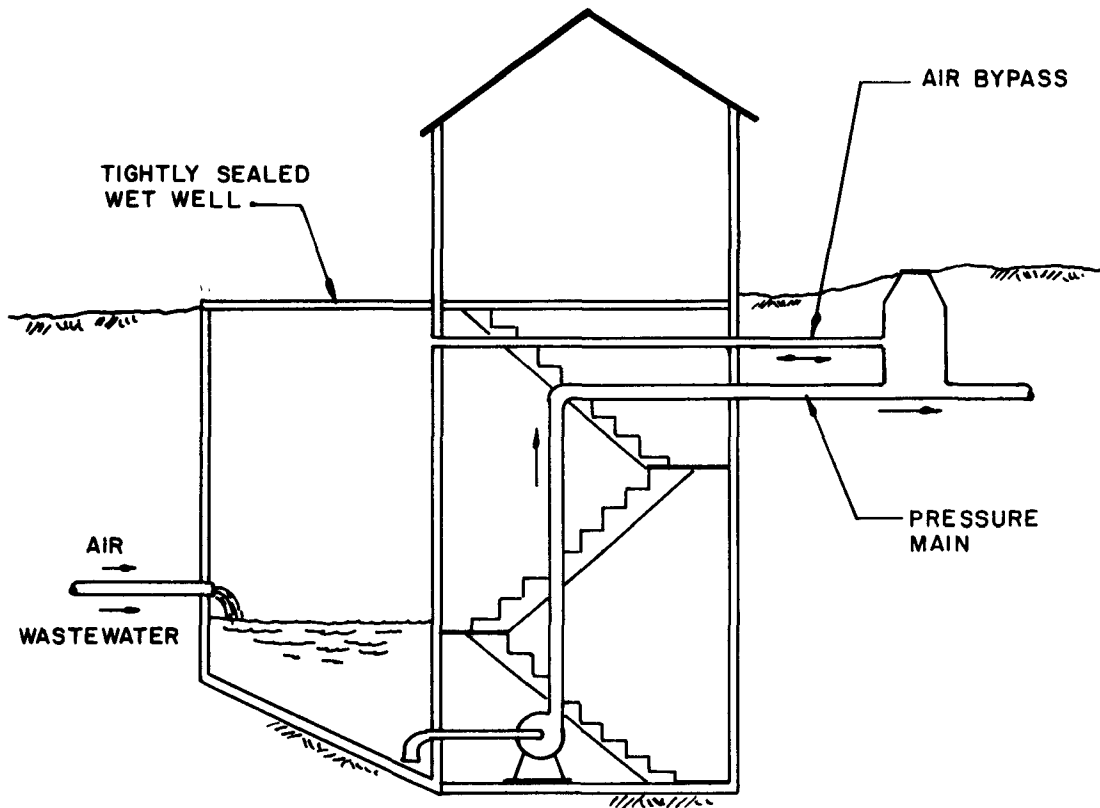
6.6.1 The Pump Station Wet Well

The wet well is seldom the site of substantial sulfide generation, even though it is often the place of odor release. The wet well can be used as a place to aerate the wastewater. Since this is a technique that can be applied in existing systems, it is discussed in Chapter 5, but the possibility should be considered when a new system is being designed. Also, a bypass for air around the pump station to control odor release from the wet well should be included in the design if the pressure main is not so long as to make this impractical. An air jumper or bypass around a siphon usually has a diameter half the diameter of the sewer (7), but around a pump station it is probably better to make it larger, perhaps 2/3 of the pipe diameter. Figure 6-3 is a schematic drawing of a pump station with an air bypass.

In stations that have no pressure main other than the riser, it may be desirable to consider air lift pumps. The double duty of an air lift in aerating and pumping the water places it in a more favorable light economically than when it is considered only as a pump.

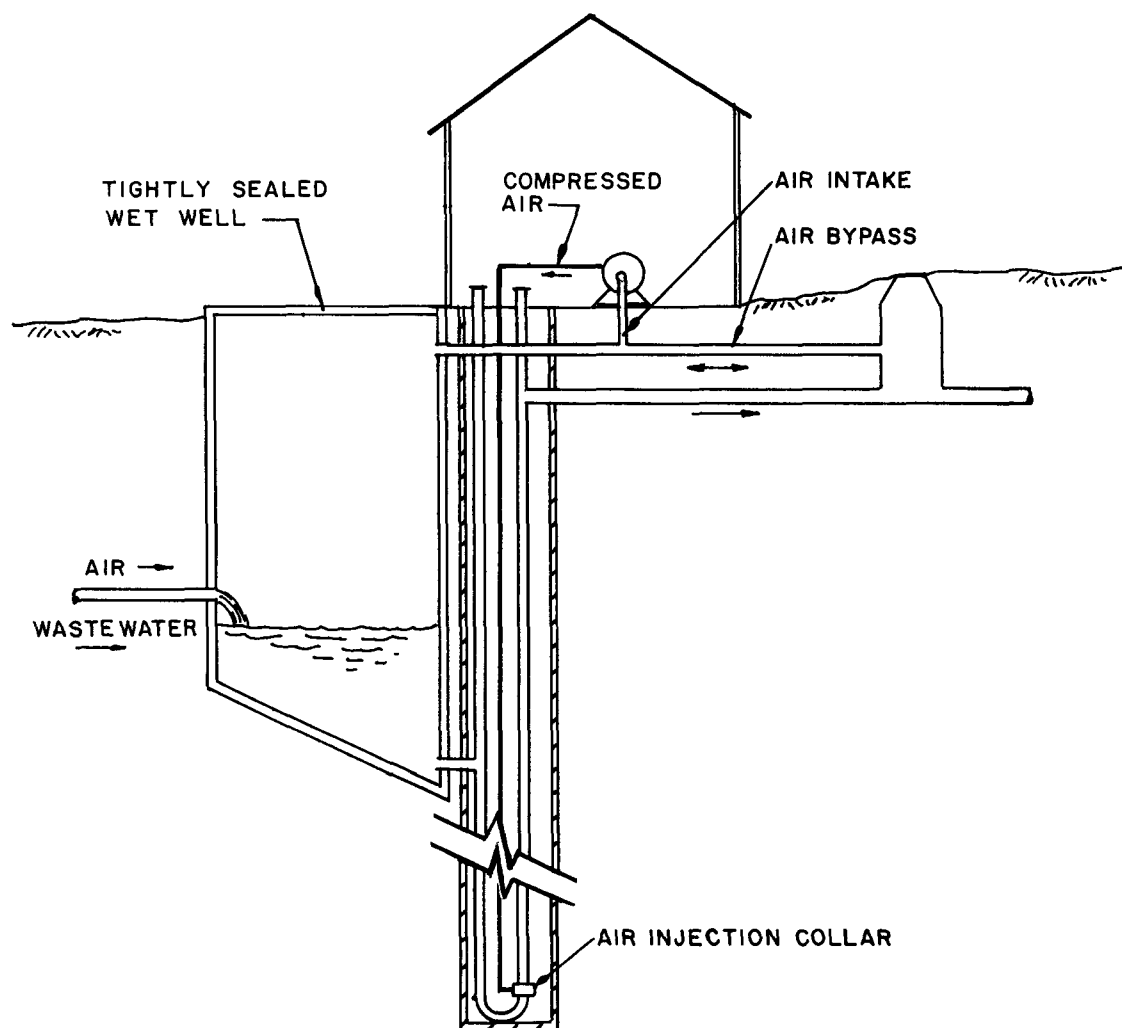
An air lift pump for a wastewater pumping station would take the form of a U-tube, with the air added near the bottom of the rising leg. The tube would probably be installed in a

FIGURE 6-3
FUNCTIONAL DRAWING OF A PUMP STATION
WITH AN AIR BYPASS



shaft, as shown in Figure 6-4. It is not necessary that the shaft be dewatered. The compressor should take suction from the air bypass connecting the wet well and the downstream sewer, thus eliminating any net discharge of air.

FIGURE 6-4
FUNCTIONAL DRAWING OF AN AIR-LIFT PUMP STATION



6.6.2 Pressure Mains—Size and Profile

Pressure mains have sometimes been made of minimum practical diameter with the aim of reducing sulfide buildup. The benefit of shorter detention time is partly offset by the greater ratio of slime-supporting pipe wall to volume of water. Within the range of pipe sizes that are practical in view of other restraints, choice of the smallest pipe size will not materially aid in solving the sulfide problem.

Since injection of compressed air into pressure mains serves so well to control sulfide generation in many situations, thought should be given to this procedure when the main

is being designed. If possible, the slope should be continuously upward. The design of the air injection system is discussed in Chapter 5. Where air injection would be ineffective because of flat slopes, or impractical because of irregular profile, plans should be made for some other way to supplement the dissolved oxygen supply.

6.7 Materials for Sewer Construction

6.7.1 Kinds of Pipe

The possibility of acid conditions resulting from oxidation of H_2S is one of the factors influencing the choice of pipe materials for sewers. If acid-proof facilities are built, then this harmful consequence of sulfide can be overcome.

Whether to construct an acid-resistant system depends upon a number of considerations. These considerations are:

1. What choices are there for pipe materials in the sizes required?
2. Will sulfide be present in the wastewater, and, if so, in what general range of concentrations?
3. Are there any factors other than acid resistance that will affect the prospective durability?
4. How do the materials compare in hydraulic smoothness?
5. What other incidental benefits and liabilities do the various kinds of pipe have?
6. What are the expected future service requirements of the sewer?
7. What are the relative costs for different kinds of conduits and how are these related to the durability of the sewer?

A cost-benefit analysis based upon the answers to the last question would permit a choice on the principle of lowest present worth of all present and future costs. This principle, rigorously applied, may not serve as a satisfactory sole criterion for design in the case of public works such as sewers having a long intended life with uncertainties in respect to future replacement possibilities, inconveniences in case of failures, etc. Decisions will vary in different communities under seemingly identical conditions. In any case, reasonable judgment would dictate a choice somewhere between such extremes as saving a small amount in calculated present worth but producing a sewer that would last only 25 years instead of 50 or 100 years, and the other extreme of spending a significant additional sum to extend to 500 or 1,000 years the life expectancy of a sewer which at lower cost would last 100 years. Beside the economic factor, there is much uncertainty about the continuing utility of any particular sewer for such long times.

In view of these considerations, it will be evident that it is not possible to provide a fixed set of rules that will automatically determine the choice of materials or the life expectancy that should be built into a sewer. Rather than to attempt any such guidelines, the principal kinds of pipe used in sewer construction will be listed and discussed, particularly in respect to susceptibility to acid attack, but with brief mention of other characteristics affecting their suitability. Protective coatings for corrodable pipe materials are discussed in other sections.

6.7.2 Vitrified Clay Pipe

This material is immune to alteration by sulfuric acid or by any other materials found in sewers. Where sulfide is expected, the use of cement mortar joints is unsatisfactory, because the action of sulfuric acid on the cement causes expansion, which may break the bells and even crack the pipe. A vitrified clay sewer properly laid and jointed will, if not disturbed by external forces, remain serviceable for a very long time.

6.7.3 Steel Pipe

If the pipe flows partly filled with wastewater containing sulfide, corrosion may occur not only by the formation of sulfuric acid, but also by the corrosiveness of H_2S toward iron in the presence of air or dissolved oxygen, producing bulky accumulations of iron sulfide. In a pipe completely filled with wastewater there is little or no corrosion even if sulfide is present, provided the pH is above 6.5 and chloride is less than 500 mg/l. Even where air is injected, corrosion due to dissolved oxygen is generally at a very slow rate, and no corrosion by acid produced from H_2S is possible unless there are air pockets where the top of the pipe is not washed by the water. If the steel pipe has a half inch or more of cement mortar lining, then it will be protected as long as it is not exposed to enough acid to destroy the protective lining.

6.7.4 Cast Iron Pipe

Cast iron pipes generally last longer than steel because the pipe wall is thicker. The corrosion of cast iron exposed to water commonly proceeds by "graphitization," in which the true iron crystals are dissolved, leaving a porous mass of carbides and silicides of iron. The surface of the iron often appears unaltered, thus giving a false impression of the true condition of the pipe. Like steel, cast iron gives good service when completely filled with wastewater at a pH of 6.5 or above, and without a high chloride content. When flowing partly filled with septic tank effluent, iron pipe is severely corroded, and may become occluded with the bulky iron sulfide corrosion product. If there is a point of turbulence, attack is accelerated. Photographs of sulfide attack in iron pipes have been published (8).

6.7.5 Wrought Iron, Malleable Iron Pipe

In atmospheric exposure, these forms of iron may have corrosion behavior different from common steel, but when submerged in water or buried in the soil, all common forms of

iron corrode at similar rates. If sulfuric acid is formed above the water, it will attack any form of iron.

6.7.6 Iron or Steel Pipe with Tar Mastic Lining

Pipe made of corrugated galvanized steel, and having a tar mastic filling the corrugations to produce a smooth internal surface has been used for sewers. Long-term durability in the presence of H_2S has not yet been established.

6.7.7 Aluminum Pipe

This metal is not resistant to corrosion under anaerobic conditions. It is not suitable for conveying wastewaters.

6.7.8 Stainless Steel Pipe

This metal, too, can suffer severe corrosion in the absence of oxygen. It is therefore not suitable for pipes to carry wastewater but is sometimes used for steps in manholes.

6.7.9 Concrete Pipe

The corrosive effects of H_2S have potential for deterioration of concrete pipe. Examples have been reported (9) (10). Nevertheless, concrete is an important sewer pipe material, and for large trunk construction it leads any other material by a wide margin. It is successfully used for small sewers as well, provided sulfide concentrations are low.

If the flow-slope relationships of sewers upstream from a given point correspond to Curve A of Figure 3-13 (adjusted for EBOD), and there are no force mains operating without proper sulfide control, then sulfide concentrations will be so low that the rate of corrosion of concrete pipe will be inconsequential. Small collecting sewers so designed, made of concrete pipe with granitic or other inert aggregate will have a life expectancy of 100 years or more. Using calcareous aggregate, the life will be much longer. Sulfide concentrations will be greater in large trunks, perhaps up to a few tenths of a mg/l, but seldom averaging more than a few hundredths of a mg/l of dissolved sulfide. The rate of corrosion will be slow because of the small values of su (slope times velocity) in the large trunks. Considering the thickness of the pipe wall in the very large pipes, a life of several centuries would be expected, or longer if calcareous aggregate is used. It is possible, however, that there may be significant attack at locations of high turbulence.

Where over-all slopes are as represented by Curve B of Figure 3-13, sulfide conditions under some circumstances may be such that bare concrete pipe made with granitic aggregate will be significantly corroded. Sulfide conditions become worse at flow-slope combinations deeper in the domain below Curve B.

It may be satisfactory to use concrete pipe under these conditions if it is made with calcareous aggregate, but the probable sulfide conditions and the rates of corrosion should be estimated. In some cases plans should be made for supplementing the oxygen sources of the stream by methods described in Section 5.1.4, or for controlling sulfide in some other way. Even with granitic aggregate, unprotected concrete may be suitable if the prospective rates of corrosion, calculated as explained in Sec. 3.6.2, are shown to be tolerable.

Sometimes the wall thickness is increased so that the concrete will outlast the corrosive forces. This is a less satisfactory strategy than to keep the same dimensions and use calcareous aggregate, where such aggregate is available. Under severe conditions calcareous aggregate pipe with extra wall thickness may be indicated.

Modifications of concrete pipe other than by use of calcareous aggregate have been tried in an effort to reduce the rate of attack. Test specimens may corrode at various rates when immersed in reservoirs of dilute acid. The principal factor determining the rates of corrosion in a sewer, however, is the rate at which acid is produced, but with the rate also varying inversely with the alkalinity of the material. Any one of the usual formulations of concrete can react as fast as the acid produced on the sewer wall can get to it. Cement type is unimportant, and the addition of a pozzolanic type of material has no effect. If a pozzolan is substituted for part of the cement, the rate of attack is increased because the alkalinity is decreased (11) (12). Attempts have been made to impregnate the pores of the concrete with wax, sulfur, tar, or resin, but these methods are unsuccessful, because acid does not reach the interior of the concrete by way of the pores, but by attacking the solid phases. Treating the pipe with SiF_4 produces a resistant surface, but it protects the concrete in the presence of H_2S only for a short time, since the surface is not impermeable.

6.7.10 Asbestos-Cement Pipe

Asbestos-cement pipe is susceptible to attack by sulfuric acid, and it therefore is not suitable where very high sulfide concentrations will prevail. However, the cement content of A-C pipe is higher than for concrete pipe with granitic aggregate, with a correspondingly lower rate of corrosion. This potential benefit may be offset by the thinner pipe wall.

6.7.11 Plastic Pipes—Homogeneous

Pipes of polyvinyl chloride (PVC), acrylonitrile-butadiene-styrene (ABS), and polyethylene (PE) have been used for sewers in smaller sizes. The materials are all resistant to sulfuric acid attack.

6.7.12 Plastic Pipes—Composite

Polyester resin is mixed with sand and then reinforced with fiberglass to make a lightweight "reinforced plastic mortar" pipe. The most vulnerable part of the composite is the glass, because water has the ability to creep along the fibers. The pipe must be manufactured so that this cannot happen. The oldest sewer made of this kind of pipe is in a trunk installed in San Jose, California, in 1966.

6.8 Protection of Concrete and Asbestos-Cement Pipe by Linings

6.8.1 Linings that Depend upon Adhesion

Since the early 1920's, experiments have been made on acid-proof linings on the inside of concrete pipe, and later asbestos-cement pipe. More money has been expended on these experiments than on any other aspect of sulfide research. Many cities have made comparative experiments with various linings, repeating fruitless efforts of others.

The reason that so many attempts have been unsuccessful is because the requirements are so exacting. Once a lined sewer is in the ground, it is expected to perform with no defects of material and no repairs, generally for 100 years or more. A successful lining material must be not only immune to acid attack; it must be impermeable to the diffusion of acid. If one installation in ten fails, even if only because of imperfect workmanship, the material is a failure. One flaw per 1,000 ft of pipe is intolerable, because it may mean expensive repairs by excavation. Furthermore, the joints must be as perfect as the rest of the pipeline. An almost-perfect lining may cause earlier failure than no lining at all, because acid migrating down an unreactive wall may cause more rapid penetration of a flaw than if the attack were more evenly distributed.

One may find examples of linings applied to the concrete surface that have remained intact for many years. In such cases, it is always found that H_2S was virtually absent.

It may take a long time for the inherent weaknesses of a material to show up. Pores of only molecular dimensions may allow the very slow diffusion of sulfuric acid, but as the underlying cement is affected the adhesion is destroyed and bulges appear, stretching the protective membrane and increasing its porosity until there is a rupture. Linings are often tested by standing a specimen of the pipe on end and filling with 5 percent sulfuric acid. Such lining tests should be conducted for a period in excess of one year.

6.8.2 Linings Keyed to the Concrete

Under this heading we do not include materials that have a presumed tie by virtue of roughness of the concrete or even interpenetration of the materials. There is no evidence that this sort of tying of the lining to the pipe wall has been significantly better than adhesion. Linings that are really locked in place have large-scale keys embedded in the concrete.

6.8.2.1 Vitriified Clay Liner Plates

The first material attempted on a large scale for lining concrete sewers was vitrified clay. Since vitrified clay itself is so durable in acid exposures, it seemed like an ideal material for this purpose. Clay plates were formed, generally about 9 by 18 inches in size, with lugs or keys formed on the back side. The plates were fastened to the inner forms before pouring the concrete to form the pipe.

The weakness of this system was the porosity of the clay. Acid diffused through, softening and expanding the cement, so that the plates cracked or the lugs were broken off.

6.8.2.2 Keyed Plastic Sheet

The principal material in this class used in sewer construction is a sheet of plasticized polyvinylchloride, about 1/16-in thick, having keys shaped like tees in cross section, running longitudinally on the sheet. The sheets are fastened on the inside forms before the pipe is poured, so that in the finished pipe the tees are imbedded in the concrete. The sheets are welded at the joints by gentle heating.

With this design, an effective lining is produced. The oldest installations (Los Angeles, California) in normal sewer construction have been in service since the early 1950's with no evidence of significant deterioration.

Difficulties have been encountered in attempting to install this kind of lining in cast-in-place structures, especially in tunnels, because it is difficult to pour the concrete and effectively imbed all of the keys. Occasionally sheets have pulled loose from the wall. No such difficulty arises in factory-made pipe. The lining may be torn by severe hydraulic stresses at points of very high velocity or turbulence, and it can be damaged by harsh cleaning tools. These difficulties can be circumvented by proper design and operation, and are not considered significant deterrents to its use.

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